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VARIABILITY IN EXPERIMENTAL BAKING
I. THE INFLUENCE OF MECHANICAL MOULDING[1]

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Series II

The adjustment of the moulder in the first series of experiments did not satisfactorily seal doughs made from certain of the flours and the machine-moulded doughs were more loosely rolled than the hand moulded. The failure of the machine to reduce variability between replicate bakings of the same flour or to bring about a substantially closer agreement between the mean volumes obtained on the same flour by different bakers may have been due to the selection of an improper adjustment of the moulder. A more extensive study of the influence of varying the adjustment of the machine on the loaf volume and texture of a series of flours was therefore undertaken and the setting selected used in a further comparative study of hand and machine moulding. Five flours, listed in Table XXVII were used for this series of experiments and,

TABLE XXVII

Description of flours used in Series II

Flour No.	Description	Bleaching treatment	Chemical analysis 13.5% moisture basis	
			Protein	Ash
5	Commercially milled, 50% patent	Alsop (nitrogen peroxide) + ¼ oz. Novadel (benzoyl peroxide) per bbl.	12.3	0.39
6	Commercially milled, bottom 60%	Unbleached	14.0	0.60
7	Commercially milled, 96% patent	1.5 gm. Agene (nitrogen trichloride) per bbl. + Alsop	13.2	0.49
8	Commercially milled, 2nd clear (bottom 15%)	3 gm. Agene per bbl.	15.4	1.05
9	Experimentally milled, straight grade	None	13.9	....

[1] *Concluded from April issue.*

with the exception of flour No. 9, were commercially milled from 1930 Canadian crop wheat. Flour No. 9 was made up by mixing and bolting together remnants of various experimentally milled flours, about 200 lb. being prepared.

TABLE XXVIII

MEAN LOAF VOLUMES OBTAINED FOR VARIOUS ADJUSTMENTS OF THE MECHANICAL MOULDER

Flour No.	Baking formula	Group *A* Sheeting rolls set at "2"			Group *B* Sheeting rolls set at "2.5"			Group *C* Sheeting rolls set at "3"		
		Depth of compression chamber at upper end in inches			Depth of compression chamber at upper end in inches			Depth of compression chamber at upper end in inches		
		a 1.43	*b* 1.36	*c* 1.28	*a* 1.43	*b* 1.36	*c* 1.28	*a* 1.43	*b* 1.36	*c* 1.28
		Mean loaf volume, cc.								
5	Simple	585	604	595	596	594	598	593	598	599
5	Bromate	635	641	636	615	629	638	632	625	621
6	Simple	519	528	532	536	534	523	524	525	532
6	Bromate	726	721	702	722	735	720	711	721	723
7	Simple	621	646	638	635	634	644	632	636	622
7	Bromate	751	740	745	747	747	734	734	732	721
8	Simple	618	628	622	634	630	626	632	614	626
8	Bromate	682	707	694	700	717	700	718	710	699
9	Simple	553	530	553	542	540	545	514	525	515
9	Bromate	654	634	618	606	607	600	564	584	557

I Experiments to Determine the Optimum Adjustment of the Moulder

In the previous moulder-setting trials, the *d* and *e* adjustments of the former plate produced too great a compression of the dough and were omitted in this series. Three adjustments of the sheeting rolls and three of the former plate were employed, six loaves being baked for each setting. The five flours were baked by the standard procedure using both the simple and bromate formulas, yielding a total of 540 loaves.

The mean loaf volumes, notes on the sealing and shape of the moulded doughs, and the mean scores for grain and texture are recorded in Tables XXVIII, XXIX and XXX respectively.

The analyses of the data pertaining to loaf volume for the different settings of the moulder are summarized in Tables XXXI, XXXII and XXXIII. Table XXXI is a complete analysis of variance for the entire experiment and brings out most of the important features. Only those portions of the analysis which have a bearing on the adjustment of the moulder will be discussed.

As pointed out above, there were three settings of the sheeting rolls designated as *A*, *B*, and *C*, and three settings of the former plate designated as *a*, *b*, and *c*. The first point of interest is the proportional effects of these adjustments.

Table XXXI shows that variations in both the setting of the sheeting rolls and the former plate produce significant differences in loaf volume. For the sheeting roll and former-plate adjustments the Z values are 1.7004 and 0.8568 respectively, each with a 5% point of 0.5520. The sheeting roll settings seem to bring about the greatest differences. Table XXXIII shows that the largest volume is obtained with the A adjustment of the sheeting rolls but the difference between A and B is not significant. Within the groups A, B, and C, the former-plate setting b gives the largest volume in each case and averaging the results we obtain Table XXXIV.

TABLE XXIX

NOTES ON SHAPE AND SEAL OF MOULDED DOUGHS FOR DIFFERENT ADJUSTMENTS OF THE MECHANICAL MOULDER

Flour No.	Baking formula	Group *A* Sheeting rolls set at "2"			Group *B* Sheeting rolls set at "2.5"			Group *C* Sheeting rolls set at "3"		
		Depth of compression chamber at upper end in inches			Depth of compression chamber at upper end in inches			Depth of compression chamber at upper end in inches		
		a 1.43	*b* 1.36	*c* 1.28	*a* 1.43	*b* 1.36	*c* 1.28	*a* 1.43	*b* 1.36	*c* 1.28
5	Simple Shape	Poor	Fair	Poor	Fair	Good	Fair	Fair	Fair	Good
	Simple Seal	Poor	Poor	Fair	Poor	Good	Good	Poor	Fair	Good
5	Bromate Shape	Poor	Good	Fair	Good	Good	Good	Fair	Fair	Fair
	Bromate Seal	Poor	Poor	Fair	Poor	Good	Good	Poor	Fair	Good
6	Simple Shape	Poor	Poor	Fair	Fair	Good	Fair	Good	Good	Good
	Simple Seal	Fair	Fair	Good	Poor	Poor	Fair	Fair	Fair	Fair
6	Bromate Shape	Poor	Fair	Poor	Fair	Good	Fair	Poor	Fair	Fair
	Bromate Seal	Poor	Poor	Poor	Poor	Fair	Good	Fair	Good	Good
7	Simple Shape	Fair	Fair	Good	Fair	Good	Good	Fair	Fair	Fair
	Simple Seal	Fair	Fair	Good	Fair	Fair	Good	Poor	Good	Good
7	Bromate Shape	Fair	Fair	Good	Poor	Fair	Good	Poor	Fair	Fair
	Bromate Seal	Poor	Poor	Fair	Fair	Good	Good	Fair	Good	Good
8	Simple Shape	Poor	Fair	Good	Poor	Poor	Poor	Poor	Fair	Fair
	Simple Seal	Poor	Fair	Good	Poor	Poor	Poor	Poor	Fair	Fair
8	Bromate Shape	Fair	Good	Good	Fair	Fair	Good	Poor	Fair	Poor
	Bromate Seal	Fair	Fair	Good	Fair	Good	Good	Poor	Fair	Poor
9	Simple Shape	Fair	Fair	Fair	Fair	Fair	Fair	Good	Good	Good
	Simple Seal	Poor	Poor	Good	Fair	Good	Good	Fair	Fair	Fair
9	Bromate Shape	Poor	Poor	Fair	Good	Fair	Good	Fair	Good	Fair
	Bromate Seal	Poor	Fair	Good	Fair	Fair	Good	Fair	Good	Poor

In so far as maximum loaf volume is concerned, there seems to be little doubt that the b setting of the former plate is the most desirable and this, combined with either the A or B adjustment of the sheeting rolls, gave equally good results.

TABLE XXX

EFFECT OF VARYING THE ADJUSTMENT OF THE MECHANICAL MOULDER. MEAN GRAIN AND TEXTURE SCORES

Flour No.	Baking formula	Group *A* Sheeting rolls set at "2"			Group *B* Sheeting rolls set at "2.5"			Group *C* Sheeting rolls set at "3"		
		Depth of compression chamber at upper end in inches			Depth of compression chamber at upper end in inches			Depth of compression chamber at upper end in inches		
		a 1.43	*b* 1.36	*c* 1.28	*a* 1.43	*b* 1.36	*c* 1.28	*a* 1.43	*b* 1.36	*c* 1.28
5	Simple	8.5	8.2	8.0	8.2	8.0	8.0	7.8	8.0	8.0
5	Bromate	9.5	9.2	9.0	9.0	9.0	9.0	9.0	9.0	9.0
6	Simple	5.0C	5.0C	4.5C	3.5C	3.2C	3.0C	3.2C	3.2C	3.2C
6	Bromate	8.0o	8.0o	8.0o	7.8o	7.8o	7.8o	7.0o	7.0o	6.5o
7	Simple	8.0	7.8	7.5	7.2	7.2	6.8	7.0	7.0	7.0
7	Bromate	9.0	8.5	8.0o	8.8	8.5	8.5	8.5	8.0o	7.8o
8	Simple	3.0C	3.0C	3.0C	3.0C	3.0C	3.0C	2.0C	2.0C	2.0C
8	Bromate	7.0C	6.8C	6.5C	6.2C	6.0C	6.0C	6.0C	6.0C	6.0C
9	Simple	7.0C&c	7.0C&c	7.0C&c	7.0C&c	7.0C&c	7.0C&c	6.8C&c	6.8C&c	6.8C&c
9	Bromate	8.0C	7.8C	7.5C	7.8C&c	7.5C&c	7.2C	7.0C	6.5C	6.0C

NOTE:—*C, coarse; c, close; o, open.*

The interaction of the five flours, shown in Table XXXI, with the *A*, *B*, *C* settings of the sheeting rolls gives interesting information. The interaction is very significant and on examining the mean volumes in Table XXXII it is obvious that this is due chiefly to flour 8, a low grade flour which yielded a sticky dough of very poor handling qualities especially when baked by the simple formula. Comparing the loaf volumes for the *B* and *C* settings the differences (*B*−*C*) are as shown in Table XXXV.

Evidently the depressing effect of the *C* setting was very marked in the case of flour No. 8 and this accounts largely for the significance of the interaction.

The interaction of the simple and bromate formulas with the *A*, *B*, *C*, settings of the sheeting rolls is also significant. This results, as will be seen from Table XXXII, from the *B* setting having given the highest mean loaf volume when the simple formula was used and from the *A* setting having given the highest mean loaf volume for the bromate formula. This seems to be related to the effect of the formula on the consistency or handling qualities of the doughs and this is reflected in the efficiency of a particular setting of the moulding machine.

The average grain and texture scores recorded in Table XXX were submitted to a variance analysis and the results are summarized in Tables XXXVII and XXXVIII. It will be observed that, as in the instance of loaf volume, the setting of the sheeting rolls and compression plate both produce significant differences in texture, the former having the greater effect as indicated by a

TABLE XXXI

EFFECT OF VARYING THE ADJUSTMENT OF THE MACHINE. ANALYSIS OF VARIANCE FOR LOAF VOLUME DATA

Variance due to	Sum of squares	Degrees of freedom	Mean square	Z	5% Pt.
Differences between flours No. 5, 6, 7, 8 and 9	913,229.1	4	228,307.3	3.5236	0.4361
Differences between simple and bromate formula	1,225,034.0	1	1,225,034.0	4.3636	0.6756
Interaction flours No. 5, 6, 7, 8, and 9, simple and bromate formula	385,271.1	4	96,317.8	3.0920	0.4361
Differences between A, B, C, setting of sheeting rolls	11,912.1	2	5,956.0	1.7004	0.5520
Differences between a, b, c, setting of former plate	2,204.2	2	1,102.1	0.8568	0.5520
Interaction (ABC)×(abc)—setting of sheeting rolls×setting of former plate	227.0	4	56.8	....	....
Interaction (No. 5, 6, 7, 8, 9×ABC) flours×setting of sheeting rolls	34,824.5	8	4,353.1	1.5437	0.3361
Interaction (No. 5, 6, 7, 8, 9×abc) flours×setting of former plate	1,675.6	8	209.4	....	....
Interaction (SB×ABC) simple and bromate formula×setting sheeting rolls	2,156.4	2	1,078.2	0.8458	0.5520
Interaction (SB×abc) simple and bromate formula×setting former plate	2,545.8	2	1,272.9	0.9328	0.5520
Second order interactions	26,089.1	52	501.7	0.4633	0.1579
Error	89,373.7	450	198.6	....	....
Total	2,694,542.6	539			

TABLE XXXII

EFFECT OF VARYING THE ADJUSTMENT OF THE MACHINE. MEAN LOAF VOLUMES WITH STANDARD ERRORS

Baking formula	Setting of sheeting rolls	Flours					S.E.	Mean	S.E. of mean
		5	6	7	8	9			
Simple	A	594.5	526.2	622.9	545.5	635.0	3.32	584.8	1.48
	B	596.0	531.0	629.8	543.3	638.1	3.32	587.6	1.48
	C	596.5	527.0	624.0	518.1	629.9	3.32	579.1	1.48
Mean of A, B and C		595.7	528.1	625.6	535.6	634.3	1.92	583.9	0.86
Bromate	A	637.4	716.0	694.1	635.2	745.3	3.32	685.6	1.48
	B	627.2	725.6	705.6	604.4	742.7	3.32	681.1	1.48
	C	625.8	718.3	709.0	568.3	731.6	3.32	670.6	1.48
Mean of A, B and C		630.1	720.0	702.9	602.6	739.8	1.92	679.1	0.86
Mean of A, B and C simple and bromate		612.9	624.0	664.2	569.1	687.1	1.36	631.5	0.61

TABLE XXXIII

EFFECT ON LOAF VOLUME OF VARIATIONS IN THE ADJUSTMENT OF THE MACHINE. MEAN RESULTS FOR ALL FLOURS BY THE SIMPLE AND BROMATE FORMULA

Group *A*			Group *B*			Group *C*			S.E.	General mean
a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*		
634.4	637.8	633.4	633.2	637.0	633.0	625.3	627.8	621.5	1.82	631.5
100.5	101.1	100.3	100.3	100.9	100.2	99.0	99.4	98.4	0.29	100.0
	635.2			634.4			624.8		1.05	631.5
	100.6			100.4			99.0		0.17	100.0

TABLE XXXIV

AVERAGE LOAF VOLUMES FOR DIFFERENT SETTINGS OF THE FORMER PLATE

	Former-plate setting			S.E.
	a	*b*	*c*	
Mean loaf volume in cc.	630.9	634.1	629.2	1.05

TABLE XXXV

DIFFERENCES IN LOAF VOLUMES FOR THE B AND C SETTINGS

	Difference in loaf volume for *B* and *C* settings				
	Flour No. 5	Flour No. 6	Flour No. 7	Flour No. 8	Flour No. 9
Simple formula	−0.5	4.0	5.8	25.2	8.2
Bromate formula	1.4	7.3	−3.4	36.1	11.1

Z value of 1.9776 and 0.9412 respectively. Table XXXVII shows that the best texture is obtained with the *A* adjustment of the sheeting rolls. Within each group the *a* setting of the former plate in each case gave the best texture, but the differences between the *a*, *b*, and *c* settings, although significant, are slight.

The interaction of the five flours and the *A*, *B*, *C* settings of the sheeting rolls is significant. This interaction is illustrated below in which the differences in the average texture by both baking formulas due to variations in these settings are compared for the different flours.

In considering these data it should be borne in mind that grain and texture were judged together. With all the flours the *A* setting of the sheeting rolls

TABLE XXXVI

DIFFERENCES IN AVERAGE TEXTURE FOR SIMPLE AND BROMATE FORMULAS COMBINED

Setting	Flour No. 5	Flour No. 6	Flour No. 7	Flour No. 8	Flour No. 9
$A-B$	0.2	0.9	0.4	0.1	0.3
$B-C$	0.0	0.5	0.5	0.7	0.2

TABLE XXXVII

EFFECT OF VARYING THE ADJUSTMENT OF THE MACHINE.
ANALYSIS OF VARIANCE FOR TEXTURE SCORE DATA

	Sum of squares	Degrees of freedom	Mean square	Z	5% Pt.
Differences between flours No. 5, 6, 7, 8, and 9	198.74	4	49.685	3.1795	0.4681
Differences between simple and bromate formula	87.22	1	87.220	3.4609	0.6965
Differences between A, B, C, setting of sheeting rolls	8.98	2	4.490	1.9776	0.5777
Differences between a, b, c, setting of former plate	1.13	2	0.565	0.9412	0.5777
Interaction, flours No. 5, 6, 7, 8 and 9 × simple and bromate formula	46.69	4	11.672	2.4553	0.4681
Interaction A, B, $C \times a$, b, c setting of sheeting rolls × setting of former plate	0.12	4	0.030	....	
Interaction flour (5, 6, 7, 8, 9) × A, B, C, setting of sheeting rolls	2.51	8	0.314	0.6475	0.3762
Interaction flours (5, 6, 7, 8, 9) × a, b, c, setting of former plate	0.26	8	0.032	....	
Interaction simple and bromate formula × A, B, C, setting of sheeting rolls	0.26	2	0.130	0.2065	0.5777
Interaction simple and bromate formula × a, b, c, setting of former plate	0.20	2	0.100	0.0754	0.5777
Error	4.47	52	0.086		
Total	350.58	89			

TABLE XXXVIII

EFFECT OF VARYING THE ADJUSTMENT OF THE MACHINE.
MEAN TEXTURE SCORES WITH STANDARD ERRORS FOR ALL FLOURS BY BOTH BAKING FORMULAS

Group A			Group B			Group C			Standard error	General mean
a	b	c	a	b	c	a	b	c		
7.3	7.1	6.9	6.8	6.7	6.6	6.4	6.4	6.2	0.093	6.7
108.5	105.9	102.5	101.8	99.8	98.5	95.5	94.4	92.6	1.4	100.0
	7.1			6.7			6.3		0.054	6.7
	105.6			100.0			94.1		0.80	100.0

gave superior grain, the cells being round and very uniform in size, although the cell walls were thick and the crumb lacked resiliency. With setting *C*, the cells were not so uniform in size or shape but the texture was more silky. There is therefore room for difference of opinion as to how these two crumb characteristics should be balanced in assigning a single score, but the uniformity of the grain was so striking in the *A* group that it appeared to outbalance the somewhat better texture of the *C* setting.

Taking the data for loaf volume and texture together the optimum adjustment of the machine would appear to be the "*Aa*" setting. However, the shape of the moulded dough and particularly the efficiency of the sealing must be taken into consideration. By reference to Table XXIX it will be observed that the *a* setting of the former plate in Group *A* did not exert sufficient compression to properly seal the doughs. In many instances the sealing was so imperfect that the baked loaves had deep V-shaped grooves along the long axis, and moulding faults were prevalent along the line of the seal in the inside of the loaf; on exerting pressure the loaves could be easily unrolled along this line. This adjustment of the former plate also gave loaves distinctly greener in crust characteristics than the *b* and *c* settings. The presence of moulding holes in the loaves would undoubtedly tend to increase the variability in loaf volume and since the *c* setting of the former plate gave the best sealing, the *Ac* adjustment of the machine was selected, namely the sheeting rolls set at "2" and the depth of the compression chamber 1.28 in. where the dough enters. The latter measurement corresponded to a depth of 1.603 in. (1-10/16 in) at the exit end, the measurement being made vertically to the drum*. This adjustment was used in all subsequent experiments.

II Machine Versus Hand Moulding by Experienced Operator

Having determined the most desirable setting of the moulder, the study reported in Part II, Series I, was repeated using the five flours listed in Table XXVII. Both the simple and bromate formulas were used and the hand- and machine-moulded loaves were again baked in pairs, and 10 loaves selected at random from each lot of replicates were judged. The mean judging scores are given in Table XXXIX.

The same general differences in the characteristics of the hand- and machine-moulded loaves were observed, namely, the less bold appearance, greener crust characteristics, more uniform grain, coarser texture, and duller crumb color of the machine-moulded loaves. The machine-moulded loaves appeared to be as variable in these characteristics as those moulded by hand.

The data given in Table XLI again show that machine moulding gives a lower loaf volume, the average difference being 41.3 cc. or 6.28% less than the loaf volume by hand moulding. With regard to absolute variability it will be observed that machine moulding gives significantly lower variability in the

**Since the preparation of this manuscript the preliminary report of Merritt, (14) holder of the A.A.C.C. Baking Fellowship, has been published. The optimum setting of the Thomson Laboratory Loaf Moulder in his experiments was found to be with the sheeting rolls set at "2" and a distance of 1 1/16 in. between the former plate and the drum measured vertically at the point of exit. This adjustment corresponds very closely to that selected on the basis of our experiments.*

TABLE XXXIX

MEAN JUDGING SCORES FOR HAND- AND MACHINE-MOULDED LOAVES BAKED FROM DIFFERENT FLOURS BY AN EXPERIENCED OPERATOR USING THE STANDARD PROCEDURE

Flour No.	Baking formula	External character				Crumb character			
		Crust color		Symmetry		Color		Grain and texture	
		Hand	Machine	Hand	Machine	Hand	Machine	Hand	Machine
5	Simple	4.8p	5.0	4.8g	4.5g	9.0	8.0	8.4	7.9
5	Bromate	4.8p	4.8p	4.5–O	5.0	9.5	8.5	8.5	8.2
6	Simple	4.8D	4.5D	3.8g	3.5g	5.0g&y	4.5dg&y	5.0C	5.7C
6	Bromate	4.8D	5.0	4.0–O	4.5g	7.0g&y	6.5dg&y	7.4–o	7.5C&o
7	Simple	5.0	4.5p	4.0g	3.8g	7.5	7.0	7.6C	7.6C&c
7	Bromate	5.0	5.0	4.2	4.8	.....	.....	7.9o	7.6
8	Simple	4.0D	4.0D	1.5g	1.2g	1.0dg&y	0.8dg&y	1.8Co	1.7C&o
8	Bromate	4.0D	4.2D	4.0	3.2	4.0d	3.5dg&y	6.3C	6.4C
9	Simple	3.0p	2.0p	3.5g	3.0g	6.5y	5.8dy	5.9C	5.5C&c
9	Bromate	3.5p	3.0p	4.2	4.0	7.0y	6.2dy	6.8o	6.9C&c

NOTE:—*p, pale; D, dark; g, underfermented characteristics; O, overfermented characteristics; gy, grey; d, dull; C, coarse; dg & y, dull grey and yellow; y, yellow; c, close; dy, dull yellow; o, open.*

instance of flours No. 5 and 6 for both the simple and bromate formulas and for flours No. 7 and 9 baked by the bromate formula. The variability obtained with flour No. 9 was particularly high in relation to the mean volumes for this flour and the reason for this will be considered later.

In Table XLII a complete analysis of variance is given for this experiment and in Table XLIV the mean loaf volumes are recorded. In Table XLII the same differences as were previously observed, were obtained between flours, between hand and machine moulding, and between the results obtained with the simple and bromate formulas. The interactions in this table are of considerable interest. The interaction, flours No. 5, 6, 7, 8, 9×hand and machine moulding is significant indicating that the two methods of moulding do not give the same relative results. The extent of this will be seen from the following values calculated from Table XLIV.

TABLE XL

DIFFERENCE BETWEEN HAND AND MACHINE MOULDING AND MEAN LOAF VOLUMES FOR BOTH METHODS OF MOULDING

	Flours				
	5	6	7	8	9
Mean loaf volume for hand and machine moulding	634.8	650.8	677.6	634.6	586.3
Difference between hand and machine results	37.6	40.4	48.8	35.0	44.2

TABLE XLI

MACHINE VERSUS HAND MOULDING BY EXPERIENCED OPERATOR.
STATISTICAL CONSTANTS PERTAINING TO LOAF VOLUME OBTAINED BY REPLICATE BAKINGS OF FIVE FLOURS BY THE STANDARD PROCEDURE

Flour No.	Baking formula	No. of loaves	Mean loaf volume, cc.					Diff. in L. V. as % L. V. Hand	Range in loaf volume, cc.		Std dev. of loaf volume, cc.		Sign. of diff. in vari. $Z/\sigma Z$	Coef. of variability in loaf volume	
			Hand x	Machine y	Response to bromate				Hand	Machine	Hand σx	Machine σy		Hand %	Machine %
					Hand	Machine	t	Hand − machine $(x-y)$							
5	Simple	50	629.4	597.2	48.4	37.7	2.69	32.2	5.12	65	50	16.76	10.34	3.381	2.66	1.73
5	Bromate	50	677.8	634.9				42.9	6.33	75	60	16.39	11.66	2.384	2.42	1.84
6	Simple	50	556.6	523.4	228.8	214.4	3.32	33.2	5.96	45	45	9.92	9.50	0.303	1.78	1.82
6	Bromate	50	785.4	737.8				47.6	6.06	85	80	21.46	17.10	1.590	2.73	2.32
7	Simple	50	640.6	594.2	122.7	118.1	0.96	46.4	7.24	70	75	14.43	16.82	1.073	2.25	2.83
7	Bromate	50	763.3	712.3				51.0	6.68	80	55	20.00	15.69	1.699	2.62	2.20
8	Simple	43	600.0	568.1	97.8	91.9	1.29	31.9	5.32	75	50	16.31	13.66	1.149	2.72	2.40
8	Bromate	49	697.8	660.0				37.8	5.42	85	85	15.88	15.84	0.017	2.28	2.40
9	Simple	50	571.9	530.5	73.0	67.3	0.87	41.4	7.24	100	75	22.59	19.82	0.916	3.95	3.74
9	Bromate	50	644.9	597.8				47.1	7.30	120	100	27.61	21.65	1.702	4.28	3.62
Entire Series																
	Simple	243	599.7	562.5	114.2	106.1	1.37	37.2	6.20	175	145	....	....	....	....	....
	Bromate	249	713.9	668.6				45.3	6.35	230	240	....	....	....	....	....
	Simple and Bromate	492	657.5	616.2				41.3	6.28	305	295	....	....	....	....	....

The mean difference between hand and machine results is 41.3 cc. and on this basis the variation in the differences for these flours is not very large. However, the experiment has been sufficiently accurate to show that this variation is significant. The order in which the flours are placed from the standpoint

TABLE XLII

MACHINE VERSUS HAND MOULDING BY EXPERIENCED OPERATOR.
ANALYSIS OF VARIANCE FOR LOAF VOLUME DATA, HAND AND MACHINE RESULTS COMBINED

Variance due to	Sum of squares	Degrees of freedom	Mean square	Z	5% pt.
Differences between flours 5, 6, 7, 8 and 9	883,977.4	4	220,994.4	3.5758	0.4358
Differences between hand and machine moulding	419,079.5	1	419,079.5	3.8958	0.6754
Differences between simple and bromate formula	2,983,955.0	1	2,983,955.0	4.8772	0.6754
Interactions					
Flours No. 5, 6, 7, 8, 9×hand and machine moulding	5,706.3	4	1,426.6	1.0543	0.4358
Flours No. 5, 6, 7, 8, 9×simple and bromate formula	947,029.6	4	236,757.4	3.6102	0.4358
Hand and machine moulding× simple and bromate formula	4,046.7	1	4,046.7	1.5756	0.6754
Second order interaction	1,017.3	4	254.3	0.1920	0.4358
Between pairs	210,923.5	482	437.6	0.4635	0.0750
Random error within pairs	83,497.8	482	173.2		
Total	5,539,233.1	983			

NOTE:—$r_{xy}=0.4328$.

of loaf volume may also be used to give a rough idea of the extent of the interaction. The hand moulding places them in the order 9, 8, 5, 6, 7 beginning with the flour of lowest loaf volume. The machine moulding places them in the order 9, 5, 8, 6, 7, but the two flours 5 and 8 which are interchanged, are close together in both cases. Obviously the extent of the interaction would have to be much greater before it could be said, from the standpoint of practical results, that hand moulding and machine moulding do not give the same relative results with different flours. However, there are evidently some slight differences in the consistency of the doughs such that they are not affected uniformly in hand and machine moulding.

The arrangement of the experiment in pairs of hand- and machine-moulded loaves enables us to eliminate from error the sum of squares for "between pairs" which in this case is quite large, and significant. The corresponding variance for between pairs, 437.6, is that portion due to influences which affect the pairs of hand- and machine-moulded loaves together. Consequently the measurement of this variance is similar to the measurement of the correlation between the hand and machine loaf volumes. The correlation coefficient can in fact be obtained from the analysis of variance table by the simple calculation

TABLE XLIII

MACHINE VERSUS HAND MOULDING BY EXPERIENCED OPERATOR.
ANALYSIS OF VARIANCE FOR LOAF VOLUME DATA, HAND AND MACHINE RESULTS SEPARATED

Variance due to	Sum of squares	Degrees of freedom	Mean square	Z	5% Pt.
Difference between hand and machine moulding	419,079.5	1	419,079.5		
Hand Moulding					
Difference between flours No. 5, 6, 7, 8, 9	460,830.3	4	115,207.6	2.8849	0.4358
Difference between simple and bromate formula	1,603,888.9	1	1,603,888.9	4.2016	0.6754
Interaction, flours No. 5, 6, 7, 8 and 9 × simple and bromate formula	491,873.1	4	122,968.3	2.9175	0.4358
Random error (x)	173,284.6	482	359.5		
Machine Moulding					
Difference between flours No. 5, 6, 7, 8 and 9	428,853.4	4	107,213.4	3.0279	0.4358
Difference between simple and bromate formula	1,384,112.8	1	1,384,112.8	4.3070	0.6754
Interaction flours No. 5, 6, 7, 8, 9 × simple and bromate formula	456,173.8	4	114,043.4	3.0588	0.4358
Random error (y)	121,136.6	482	251.3		
Total	5,539,233.0	983			

TABLE XLIV

MACHINE VERSUS HAND MOULDING BY EXPERIENCED OPERATOR.
MEAN LOAF VOLUMES WITH STANDARD ERRORS BASED ON HAND AND MACHINE RESULTS SEPARATED

Baking formula	Flour 5	Flour 6	Flour 7	Flour 8	Flour 9	S.E. of 5, 6, 7, 8, 9	Mean	S.E. of mean
Hand Moulding								
Simple	629.4	556.6	640.6	600.0	571.9	2.68	599.7	1.21
Bromate	677.8	705.4	763.3	697.8	644.9	2.68	713.9	1.21
Simple and bromate	653.6	671.0	702.0	652.1	608.4	1.90		
General mean							657.5	0.85
Machine Moulding								
Simple	597.2	523.4	594.2	562.1	530.5	2.24	562.5	1.01
Bromate	634.9	737.8	712.3	660.0	597.8	2.24	668.6	1.01
Simple and bromate	616.0	630.6	653.2	617.1	564.2	1.58		
General mean							616.2	0.71

$r_{xy} = \frac{437.6 - 173.2}{437.6 + 173.2} = 0.4328$. This is in reality an *intra class* correlation coefficient and for positive correlations agrees very closely with the simple product moment coefficient. The significance of this coefficient is the same as the significance of variance for "between pairs" and is therefore given in the analysis of variance table. In Table XLIII the total sum of squares for the experiment has been divided again into portions representing hand and machine moulding, but in so doing the two estimates of error are larger than the one estimate in Table XLII due to the necessary sacrifice of the sum of squares for "between pairs". However the random errors x and y in this table represent the variations in loaf volume within the group of 50 loaves baked for each flour and consequently may be compared in order to obtain some measure of the reduction in variability due to the use of the machine moulder. Comparing the variances directly, 359.5 for hand moulding and 251.3 for machine moulding, the Z value is 0.2162 and the 5% point is only 0.0750 so that this difference must be considered significant. Again, however, we must consider the correlation between variability and loaf volume and it is interesting to apply a test to the standard deviations corrected for the corresponding loaf volumes; which is similar to testing the significance of the difference between the coefficients of variability. The calculations are given in Table XLV.

TABLE XLV

	Actual standard deviation	Standard deviation relative to loaf volumes	Z	5% Pt.
Hand moulding	18.96	18.36	0.1141	0.0750
Machine moulding	15.85	16.38		

The Z value is obtained from the difference between the natural logarithms of the standard deviations. The 5% point is the same as that used for testing the difference between the variances. There seems to be no doubt therefore as to the significance of the reduction in variability due to machine moulding. The amount of this reduction however is actually not very great as will be seen from the coefficients of variability which are 2.88% for hand moulding and 2.57% for machine moulding. The new adjustment of the machine, which gave better and more uniform sealing of the doughs is apparently a distinct improvement over the setting used in Series I, which showed no significant reduction in variability by machine moulding when the standard deviations were corrected for the differences in mean loaf volume.

The statistical constants given in Table XLVI were taken from a series of analyses of variance, one for each flour, the results for the simple and bromate formulas being treated separately in the manner previously described in the discussion of Table XIX, Part II, Series I. It will be observed that the loaf volume results by the bromate formula gave, in general, significantly higher

TABLE XLVI

MACHINE VERSUS HAND MOULDING BY EXPERIENCED OPERATOR
STATISTICAL CONSTANTS OBTAINED FROM VARIANCE ANALYSES OF LOAF VOLUME DATA FOR REPLICATE BAKINGS OF FIVE FLOURS BY THE STANDARD PROCEDURE

Flour No.	Standard deviation		Significance of random errors		Significance of difference between hand and machine loaf volume				Correlation between loaf volumes by hand and machine				$\frac{Z_1-Z_2}{\sigma(Z_1-Z_2)}$
	Simple	Bromate	Simple vs. bromate		Simple		Bromate		Simple		Bromate		
			$Z+$	Z/σ_Z	Z	5% Pt.	Z	5% Pt.	r_{xy}	Z_1/σ_{Z_1}	r_{xy}	Z_2/σ_{Z_2}	
5	11.26	13.03	0.1461+	1.23	2.6600	0.6980	2.7995	0.6980	0.360	2.64	0.178	1.01	
6	8.18	18.85	0.8351+	5.84	3.0117	0.6980	2.5366	0.6980	0.074	0.525	0.305	2.20	
7	11.41	16.08	0.3440+	2.41	3.0121	0.6980	2.7627	0.6980	0.481	3.64	0.216	1.53	
8	10.31	9.41	0.0916−	0.61	2.6631	0.7022	2.9901	0.6985	0.541	3.93	0.655	5.44	
9	10.81	17.38	0.4749+	3.32	2.9534	0.6980	2.6053	0.6980	0.746	6.76	0.519	4.03	
Entire series	10.46	15.34	0.6917+	10.74	2.8754	0.4059	2.6945	0.4057	0.559	9.69	0.349	5.68	2.93

NOTE: + *sign indicates bromate formula gives greater variability; x, loaf volume by hand moulding; y, loaf volume by machine moulding.*

TABLE XLVII

STATISTICAL CONSTANTS PERTAINING TO LOAF VOLUME OBTAINED BY REPLICATE BAKINGS OF FLOUR 7, SIMPLE FORMULA BY BAKER *A* ON FIVE CONSECUTIVE DAYS

Day	No. of loaves	Mean loaf volume, cc.			Diff. in loaf volume as % L. V. hand	Range in loaf volume, cc.		Standard deviation loaf volume, cc.		Significance of difference in variability	Coefficient of variability in loaf volume, %	
		Hand x	Machine y	Hand − Machine		Hand	Machine	Hand σ_x	Machine σ_y	Z/σ_Z	Hand	Machine
1	50	640.6	594.2	46.4	7.24	70	75	14.43	16.82	1.072	2.25	2.83
2	50	629.7	577.6	52.1	8.27	65	40	16.02	8.76	4.224	2.54	1.52
3	50	638.6	583.0	55.6	8.71	65	45	15.26	12.03	1.665	2.38	2.06
4	50	622.2	566.8	55.4	8.90	50	45	11.76	10.64	0.701	1.89	1.88
5	50	625.4	569.1	56.3	9.00	70	60	16.12	12.56	1.746	2.58	2.21
5 days combined		630.9	578.2	52.7	8.35	100	90	...	...	...	...	...

experimental errors than those for the simple formula. The significance of the differences between the loaf volumes obtained by hand and machine moulding is quite similar for the different flours and for the two baking formulas. The intra-class correlations are of particular interest since they measure the extent to which low or high loaf volumes by hand and machine moulding are associated and hence are an indication of the extent of systematic variations between the different pairs due to uncontrolled factors in the baking procedure. The majority of these correlations are significant, the bromate series, taken as a whole, giving a significantly higher correlation than the simple formula. The correlations for flour No. 9 are particularly high, 0.746 and 0.519 for the simple and bromate formula respectively, and it will be recalled that the variability in loaf volume was also very high for this flour. This flour was synthesized from remnants of a large number of experimentally milled flours and it is quite probable that incomplete mixing was responsible for the above results.

III Effect of Machine Moulding on Secular Variation in Loaf Volume

In the baking laboratory comparisons between flours or methods of baking are often made on the basis of results obtained on different days or at different times in the same day. Experience has indicated that, for some reason unknown at present, there may be secular variation not only from day to day, but also during the course of any one day. Several reasons might be advanced to account for this. The baker may not handle the doughs in a uniform manner due perhaps to changing disposition or fatigue and, if such is the case, a mechanical moulder which reduces the variability due to the personal element would tend to eliminate secular variation. On the other hand, variations in punching, in different lots of yeast, or in the temperature of the baking cabinet and oven from day to day might be responsible for the variations between days. Similarly, changing disposition of the operator in punching, variations in the yeast suspension on standing, or lack of uniformity in the temperature of the baking cabinet or oven, resulting in place differentiation would account for the trends within days. In these instances machine moulding would not smooth out the baking results obtained on different days or at different intervals within one day.

An experiment was designed to determine the value of machine moulding in reducing secular variation. Flour No. 7 was baked by the simple formula on five consecutive days by baker *A*. Fifty pairs of loaves were baked each day, the pairs consisting of one loaf moulded by hand and one by machine for each of the fifty replicate mixings, the consecutive pairs of loaves being placed in the same position in the fermentation cabinet each day.

Table XLVII gives the mean loaf volumes obtained for hand and machine moulding on each of the five days, with the standard deviations and coefficients of variability, showing the influence of machine moulding on the variability within days. The mean difference between the hand and machine loaf volume increases from the first to the fifth day, and, expressing these differences in per cent of the corresponding mean loaf volumes for hand moulding, there is a

definite trend from the first to the fifth day. The figures for the consecutive days are 7.24%, 8.27%, 8.71%, 8.90% and 9.00%. It will also be observed that machine moulding gave a significantly lower variability than hand moulding on the second, third and fifth days.

Turning to the analysis of variance given in Table XLVIII the difference between the hand and machine values is expressed in terms of the interaction between days with hand and machine moulding. The Z value of 0.5722 is just greater than the 5% point and may therefore be considered significant. The interaction however is not great and from Table XLVII it is obviously due chiefly to the results for Day 1.

The total sum of squares given in Table XLVIII has been divided into various components which give interesting information. The first component is that due to differences between the time intervals within days and the second is due to the differences between the days. These are both significant although the latter is much larger and more significant than the former.

From Table LIII it will be observed that the standard error of the mean values for the combined hand and machine results is 1.22 for single days,

TABLE XLVIII

ANALYSIS OF VARIANCE FOR LOAF VOLUME DATA, HAND AND MACHINE RESULTS COMBINED, OBTAINED BY REPLICATE BAKINGS OF FLOUR 7 ON FIVE CONSECUTIVE DAYS BY BAKER *A*

Variance due to	Sum of squares	Degrees of freedom	Mean squares	Z	5% Pt.
Differences between baking intervals within days	13,331.7	49	272.1	0.4169	0.1750
Differences between days	37,413.0	4	9,353.2	2.1856	0.4415
Difference between hand and machine moulding	347,899.4	1	347,899.4	3.9936	0.6791
Interactions					
Intervals of baking within days × days	51,257.4	196	261.5	0.3971	0.1178
Intervals of baking within days × hand and machine moulding	8,786.7	49	179.3	0.2084	0.1750
Between days × hand and machine moulding	1,484.6	4	371.2	0.5722	0.4415
Error	23,165.7	196	118.2		
Total	483,338.5	499			

so that a difference between any two of the means of about 4 cc. may be considered significant. The range between the daily means for the five days is 22.9 cc. so that the differences are very large in proportion to the standard error. Considering the hand and machine results separately, the ranges between the daily means are 18.4 and 27.4 cc. respectively. Furthermore, arranging the days in order of increasing loaf volume we have the same order,

namely 4, 5, 2, 3, 1 for both hand and machine moulding. Evidently some systematic factor or factors are operating which affect both hand and machine results to almost the same extent. The interaction between days with hand and machine moulding, however, is just significant which indicates that the hand and machine results are not affected in an exactly similar way, but the difference is very slight. These considerations make it perfectly obvious that machine moulding does not reduce the day to day differences, implying that the "moulding personality" of baker *A* did not contribute materially to the different results which he obtained on different days. The present investigation does not throw any light on the causal factors. They may, of course, be due to a different daily disposition of the baker in the handling of the doughs during punching or to lack of uniformity in the yeast from day to day. The temperatures of the mixed doughs and of the baking cabinet and oven were carefully controlled and, while small local fluctuations in temperature might conceivably be in part responsible for secular variations within days it seems altogether improbable, in view of the control exercised, that temperature variations are responsible for the daily differences.

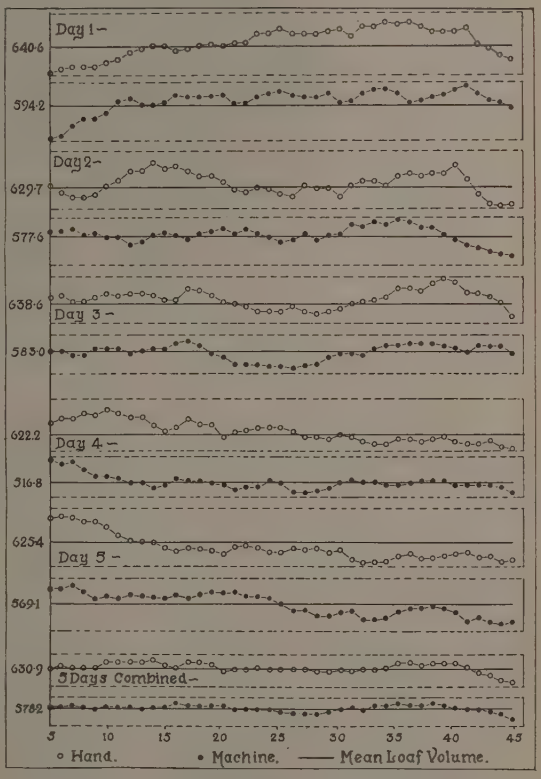

FIG. 1. *Graphs illustrating the trend in loaf volume for baking intervals within days. The points plotted are the moving averages for each ten consecutive loaf volumes.*

Regarding the time variation throughout any one day, this is undoubtedly significant as evidenced by the Z value of 0.4169 with a 5% point of 0.1750 given in Table XLVIII. The trend within days is illustrated in Fig. 1 in which the moving average for each 10 consecutive loaf volumes is plotted separately for the hand and machine results for each day and also for the five days combined. It will be observed that the moving averages are not equally distributed above and below the mean. This is due to the fact that, in the calculations, the values for the baking intervals at the beginning and end of the

day are not used as frequently as those in the central portion of the bake. The interaction between days and times of baking (Table XLVIII) is significant which means that the daily trends are not alike on different days. This is illustrated in Fig. I. For example on Day 1, the first loaves baked were lower in volume than the mean for the day, while on Day 4, and Day 5, they were higher. The daily trends are similar to the extent that there is a more or less uniform tendency for the last loaves baked to be lower in loaf volume. These trends persist in the machine results and are more marked on some days than others. The trend curves for the five days combined deviate but slightly from the mean values. Since the loaves for the corresponding intervals for each day were placed in the same positions in the cabinet and oven, there is no definite indication of any constant localized differences attributable to place differentiation in the cabinet.

The conclusions from this experiment are fairly obvious. Machine moulding does not reduce the day to day variation in loaf volume nor does it eliminate the trends which occur within days. This secular variation is an important factor in experimental baking and, until the causal factors are elucidated and these variations eliminated, should be taken into account in the planning of baking experiments.

IV Punching versus Moulding as Factors in Producing Variability Between Bakers

In the baking test the personal element may introduce variability not only in the moulding of the dough, but also in the punching. A comparison of the hand and machine results for the five bakers (reported in part IV, Series I) showed no appreciable reduction in the differences between the bakers through the use of a mechanical moulder, suggesting that punching personality was a contributing factor. Accordingly an experiment was planned in order to determine the relative importance of these two operations in producing variability. Four bakers, *A*, *C*, *D*, and *E*, whose experience has been previously detailed, were employed. Two hundred loaves of flour No. 7 were baked by the simple formula on three consecutive days. Two hundred grams of flour was mixed at one time, the dough divided after mixing, and treated as pairs, one dough being hand moulded and the other machine moulded. The scheme for one day's bake was as follows:

Series *A*, 50 mixings { 50 loaves *A* punching, *C* moulding by hand
50 loaves *A* punching, *C* moulding by machine

Series *B*, 50 mixings { 50 loaves *C* punching, *C* moulding by hand
50 loaves *C* punching, *C* moulding by machine.

The above scheme was repeated with bakers *D* and *E*. Baker *A* was used in punching the doughs for the other bakers because of his greater experience. The means, standard deviations and coefficients of variability are given in Table L.

The influence of moulding on producing variability in loaf volume between bakers will first be considered. For this purpose, the five days work by baker *A*, reported in the previous section, has been combined with that portion

of the subsequent bakes made on three consecutive days in which *C*, *D*, and *E* moulded and *A* punched, representing a total of 800 loaves. The variance analysis for the hand and machine results combined is given in Table LI. The second variance given in the table, with a *Z* value of 2.9155 and a 5% point of 0.6760 represents the significance of the difference between the mean volume obtained by *A*, and the mean for *C*, *D*, and *E* combined. The mean for *A* is 604.5 cc. and for *C*, *D*, and *E* is 588.0 cc. The difference between these values is very significant and may be due to the differences in moulding by experienced versus less experienced operators. However, part of the difference observed may be due to the day effect which has previously been noted. The *Z* values for the differences between bakers *C*, *D*, and *E* moulding, and for the difference between days for baker *A* have practically the same degree of significance.

The interactions given in Table LI are instructive. The first shows baker *A* obtained results for hand and machine moulding which were significantly different from those obtained on the average by *C*, *D*, and *E*. This is illustrated in Table XLIX.

TABLE XLIX

RESULTS FOR HAND AND MACHINE MOULDING OBTAINED BY BAKER *A* COMPARED WITH THOSE OBTAINED BY *C*+*D*+*E*

	Mean loaf volume in cc.		
	A 5 days combined	*C*−*D*+*E*	Difference between *A* and *C*−*D*−*E*
Hand moulded	630.9	603.2	27.7
Machine moulded	578.2	572.9	5.3
Hand−machine	52.7	30.3	22.4

For machine moulding the baking procedure in the two groups varied only to the extent that different operators placed the dough in the machine and in this instance, the mean results for *A* and for *C*, *D*, and *E* combined differ only by 5.3 cc. In the results for hand moulding, however, the personal factor entered into the manipulation of the dough during moulding, and the difference between the two groups is 27.7 cc. Evidently the less experienced operators handle the dough in such a manner as to reduce the loaf volume, thus decreasing the difference between the hand and machine results.

The next interaction given in Table LI shows that the three bakers *C*, *D*, and *E* secure different relative results for hand and machine moulding. This is in striking contrast to the interaction of *A*'s results for five days with hand and machine moulding which, as pointed out in a previous analysis, was just significant. A comparison of these two results is shown in Table LII, by the mean values taken from Table LIII.

The variable results for *C*, *D*, and *E* are evidently due to the low volume obtained by *C* and *E* in hand moulding.

The division in Table LV of the total sum of squares into the two chief portions, one for hand moulding and one for machine moulding enables us to test again the effect of machine moulding in reducing random error and the

TABLE L

PUNCHING VERSUS MOULDING AS FACTORS PRODUCING VARIABILITY BETWEEN BAKERS

SUMMARY OF DATA PERTAINING TO LOAF VOLUMES OBTAINED BY REPLICATE BAKINGS OF FLOUR NO. 7, USING THE SIMPLE FORMULA

Baker	No. of loaves	Mean loaf volume, cc.			Diff. in L. V. as % of L. V. hand	Range in loaf volume, cc.		Standard deviation of loaf volume, cc.		Sign. of diff. in Vari. $Z/\sigma Z$	Coefficient of variability	
		Hand x	Machine y	Hand – machine		Hand	Machine	Hand σx	Machine σy		Hand %	Machine %
A punch *C* mould	50	596.2	578.2	18.0	3.02	85	60	17.20	15.26	0.838	2.88	2.64
C punch *C* mould	50	586.6	562.8	23.8	4.06	55	65	14.18	16.53	1.099	2.42	2.94
A punch *D* mould	50	626.7	571.0	55.7	8.89	95	70	19.42	16.58	1.106	3.10	2.90
D punch *D* mould	50	635.6	589.3	46.3	7.28	75	80	16.73	19.39	1.033	2.63	3.29
A punch *E* mould	50	586.6	569.5	17.1	2.92	80	90	17.34	15.84	0.632	2.96	2.78
E punch *E* mould	50	574.3	558.8	15.5	2.70	80	75	15.54	14.62	0.426	2.71	2.62

TABLE LIII

EFFECT OF PUNCHING ON PRODUCING VARIABILITY BETWEEN BAKERS

MEAN LOAF VOLUMES WITH STANDARD ERRORS OBTAINED BY *A* PUNCHING, WITH *A*, *C*, *D* AND *E* MOULDING

	Baker *A*						Baker *A*		Baker *A* punching with bakers *C*, *D* and *E* moulding						Entire experiment	
	Mean loaf volume, cc.						All days combined		Mean loaf volume, cc.							
	Day 1	Day 2	Day 3	Day 4	Day 5	Std. error	Mean L. V. cc.	Std. error cc.	*C*	*D*	*E*	Std. error	*C*+*D*+*E* Mean	*C*+*D*+*E* Std. error	Mean L. V. cc.	Std. error cc.
Hand	640.6	629.7	638.6	622.2	625.4	2.30	630.91	1.03	596.2	626.7	586.6	2.30	603.16	1.33	620.50	0.81
Machine	594.2	577.6	583.0	566.8	569.1	2.02	578.15	0.90	578.2	571.0	569.5	2.02	572.93	1.16	576.19	0.71
Hand + machine	617.4	603.6	610.8	594.5	597.2	1.22	604.53	0.55	587.2	598.8	578.0	1.22	588.04	0.71	598.34	0.43

differences between days and between bakers. It will be remembered that, with the new moulder setting, a significant reduction in the random error was brought about by the use of the machine moulder with an experienced baker working on five different flours. With the introduction in the experiment now

TABLE LI

EFFECT OF PUNCHING ON PRODUCING VARIABILITY BETWEEN BAKERS. ANALYSIS OF VARIANCE FOR LOAF VOLUME DATA, HAND AND MACHINE RESULTS COMBINED, OBTAINED BY *A* PUNCHING AND *A*, *C*, *D* AND *E* MOULDING

Variance due to	Sum of squares	Degrees of freedom	Mean square	*Z*	5% Pt.
Differences between hand and machine moulding	392,675.22	1	392,675.22	3.9364	0.6760
Differences between Experiments					
I. Between baker *A* (all days combined) vs. bakers *C*, *D*, *E*	50,964.41	1	50,964.41	2.9155	0.6760
II. Between bakers *C*, *D* and *E*	21,736.17	2	10,868.08	2.1428	0.5524
III. Between days 1 to 5 for baker *A*	37,413.00	4	9,353.25	2.0678	0.4367
Interactions of Hand and Machine Moulding					
I. Between baker *A* (all days combined) and bakers *C*, *D* and *E*	23,778.30	1	23,778.30	2.5343	0.6760
II. Between bakers *C*, *D* and *E*	24,293.53	2	12,146.76	2.1985	0.5524
III. Between days 1 to 5 for baker *A*	1,484.53	4	371.13	0.4543	0.4367
Difference between pairs	124,563.82	392	317.76	0.3767	0.0832
Random error within pairs	58,638.42	392	149.59		
Total	735,547.40	799			

TABLE LII

COMPARISON OF RESULTS OF BAKERS *A*, *C*, *D*, AND *E* FOR HAND AND MACHINE MOULDING

	Mean loaf volume in cc.							
	A punching and moulding, 5 days results					*A* punching and *C*, *D* and *E* moulding		
	1	2	3	4	5	*C*	*D*	*E*
Hand moulding	640.6	629.7	638.6	622.2	625.4	596.2	626.7	586.6
Machine moulding	594.2	577.6	583.0	566.8	569.1	578.2	571.0	569.5
Difference	46.4	52.1	55.6	55.4	56.3	18.0	55.7	17.1

TABLE LIV

	Mean square	Standard deviation cc.	Mean L. V. cc.	Std. dev. relative to L. V. cc.	*Z*	5% Pt.
Hand moulding	264.00	16.25	620.5	15.76	0.0564	0.0842
Machine moulding	203.35	14.26	576.2	14.81		

being described, of three inexperienced bakers, the effect of machine moulding should be greater if the element of inexperience in moulding is an important factor contributing to variability between replicates. In this case the result shown in Table LIV was obtained. Here there is no significant reduction in variability relative to mean loaf volume.

TABLE LV

EFFECT OF PUNCHING ON PRODUCING VARIABILITY BETWEEN BAKERS. ANALYSIS OF VARIANCE FOR LOAF VOLUME DATA, HAND AND MACHINE RESULTS SEPARATED, OBTAINED BY A PUNCHING AND A, C, D AND E MOULDING

Variance due to	Sum of squares	Degrees of freedom	Mean square	Z	5% pt.
Differences between hand and machine moulding	392,675.22	1	392,675.22		
Hand Moulding					
Difference between baker A (all days) and bakers $C+D+E$	72,182.95	1	72,182.95	2.8055	0.6760
Differences between days for baker A	14,304.66	4	3,576.16	1.3027	0.4367
Differences between bakers C, D & E	43,873.48	2	21,936.74	2.2096	0.5524
Random error(x)	103,488.91	392	264.00		
Machine Moulding					
Difference between baker A (all days) and bakers $C+D+E$	25,559.77	1	25,559.77	1.2665	0.6760
Differences between days for baker A	24,592.86	4	6,148.25	1.7046	0.4367
Differences between bakers C, D and E	2,156.22	2	1,078.11	0.8341	0.5524
Random error (y)	79,713.33	392	203.35		
Total	735,547.40	799			

TABLE LVI

MEAN LOAF VOLUMES FROM TABLE LIII

	5 days results. A punching and moulding by hand	3 days results. A punching and bakers C, D and E moulding by hand
	630.0 cc.	603.2 cc.
	C, D and E hand moulding and A punching	C, D and E moulding with machine and A punching
Baker C	596.2 cc.	578.2 cc.
Baker D	626.7 cc.	571.0 cc.
Baker E	586.6 cc.	569.5 cc.

The significance of the differences between bakers however is much greater for hand moulding, the Z values being 2.2096 and 0.8341 for hand and machine moulding respectively each with a 5% point of 0.5524. It will be remembered that baker A did the punching throughout and therefore with regard to the

machine-moulded loaves the other operators contributed only by putting the dough through the mechanical moulder. The effect of this shows up in the mean values (Table LVI) taken from Table LIII.

In the first set of results a day influence may have entered in but it appears that the average effect of the inexperienced bakers moulding by hand is to reduce the mean loaf volume. In the second set of results it seems evident that the effect of different bakers moulding is to introduce greater variability, and hence "moulding personality" is an important factor contributing to the differences in mean loaf volume obtained by different bakers.

The next analysis given in Table LVII, with mean values in Table LVIII begins the direct comparison of the effects of punching and moulding. This comparison is based on the results from baking 600 loaves according to the scheme already outlined. Half of the loaves were punched by baker *A* and moulded by *C*, *D* and *E*; the other half were punched and moulded by *C*, *D* and *E*. As in previous studies the loaves were baked in pairs, one being moulded by hand, and the other by machine.

TABLE LVII

PUNCHING VERSUS MOULDING AS FACTORS IN PRODUCING VARIABILITY.
ANALYSIS OF VARIANCE FOR LOAF VOLUME DATA, HAND AND MACHINE RESULTS COMBINED FOR BAKER *A* PUNCHING AND *C*, *D* AND *E* MOULDING VERSUS *C*, *D* AND *E* PUNCHING AND MOULDING

Variance due to	Sum of squares	Degrees of freedom	Mean square	*Z*	5% Pt.
Difference between bakers *C*, *D* and *E*	119,731.61	2	59,865.80	2.8906	0.5537
Difference between *A* punching and *C*, *D* and *E* punching	1,799.20	1	1,799.20	1.1382	0.6771
Difference between hand and machine moulding	129,448.28	1	129,448.28	3.2762	0.6771
Interaction, *A* and *C*, *D* and *E* punching vs. hand and machine moulding	110.08	1	110.08	....	0.6771
Interaction, bakers *C*, *D* and *E*, vs. *A* and *C*, *D* and *E* punching	21,836.22	2	10,918.11	2.0397	0.5537
Interaction bakers *C*, *D* and *E* vs. hand and machine moulding for baker *A* punching	24,293.53	2	12,146.76	2.0930	0.5537
Interaction, bakers *C*, *D* and *E* vs. hand and machine moulding for bakers *C*, *D* and *E* punching	12,617.82	2	6,308.91	1.7655	0.5537
Difference between pairs	111,643.19	294	279.74	0.3603	0.0961
Random error within pairs	54,290.79	294	184.66		
Total	475,770.72	599			

The difference between the bakers *C*, *D*, and *E* is highly significant, the mean loaf volumes being 581.0, 605.6 and 572.3 respectively, for the hand and machine results combined. The effect of punching is significant as indicated by the *Z* value of 1.1382 with a 5% point of 0.6771. This is clearly brought out by comparing the difference between the mean loaf volume for 300 loaves punched by *A* and by *C*, *D*, and *E* respectively, the moulding having been done in both cases by bakers *C*, *D*, and *E*. These values are 588.0 and 584.6 cc.

TABLE LVIII

EFFECT OF PUNCHING VERSUS MOULDING IN PRODUCING VARIABILITY BETWEEN BAKERS. MEAN LOAF VOLUMES WITH STANDARD ERRORS

	Method of moulding	Baker *C*	Baker *D*	Baker *E*	S. E. of *C*, *D* or *E*	Mean of *C*, *D* and *E*	S.E. of mean
A punching and *C D* or *E* moulding	Hand	596.2	626.7	586.6	1.92	603.2	1.11
	Machine	578.2	571.0	569.5	1.92	572.9	1.11
	Hand + machine	587.2	598.8	578.0	1.36	588.0	0.78
C, *D* or *E* punching and *C*, *D*, or *E* moulding	Hand	586.6	635.6	574.3	1.92	598.8	1.11
	Machine	562.8	589.3	558.8	1.92	570.3	1.11
	Hand + machine	574.7	612.4	566.6	1.36	584.6	0.78
	Means, *C*, *D* and *E*	581.0	605.6	572.3	0.96	586.3	0.55

respectively and a difference of 2.4 cc. may be considered significant. The difference is not very great chiefly due to the "punching personality" of baker *D* producing a higher loaf volume than *A*. The best comparison is therefore for each of the bakers with baker *A* using the results obtained by machine moulding only in order to eliminate any possible effect of hand moulding. The results are:

A punching, 578.2 cc. *C* punching, 562.8 cc. Difference, +15.4 cc.
A punching, 571.0 cc. *D* punching, 589.3 cc. Difference, −18.3 cc.
A punching. 569.5 cc. *E* punching, 558.8 cc. Difference, +10.7 cc.

A difference between these values of 6 cc. may be considered significant so that these results leave no doubt as to the effect of individuality in punching. This result is shown in Table LIX as an interaction between bakers *C*, *D* and *E* with *A*, and *C*, *D*, and *E* punching. For machine moulding the *Z* value is 1.7048 and the 5% point is 0.5537. In Table LVII the same interaction is shown for hand and machine moulding combined and is highly significant. The actual values taken from Table LVIII are:

A punching, 587.2 cc. *C* punching, 574 7 cc. Difference, +12.5 cc.
A punching, 598.8 cc. *D* punching, 612.4 cc. Difference, −13.6 cc.
A punching, 578.0 cc. *E* punching, 566.6 cc. Difference, +11.4 cc.

and a difference between any pair of values of slightly over 4 cc. may be considered significant.

The significant interactions for hand and machine moulding with the different bakers given in Table LVII show that they do not obtain the same relative results by hand and machine moulding. The extent of this is clearly shown by tabulating the differences between the hand and machine results as in Table LX. These differences in relative results are very striking and are due chiefly to baker *D*. It will be noted that the only case in which baker *D* obtained results comparable with either of the other bakers was when *A* punched the dough and *D* merely placed it in the machine for moulding. The

TABLE LIX

PUNCHING VERSUS MOULDING AS FACTORS IN PRODUCING VARIABILITY.
ANALYSIS OF VARIANCE FOR LOAF VOLUME DATA, HAND AND MACHINE RESULTS SEPARATED FOR BAKER *A* PUNCHING AND *C*, *D* AND *E* MOULDING VERSUS *C*, *D* AND *E* PUNCHING AND MOULDING

Variance due to	Sum of squares	Degrees of freedom	Mean square	*Z*	5% Pt.
Difference between hand and machine moulding	129,448.28	1	129,448.28		
Hand Moulding					
Difference between bakers *C*, *D* and *E*	142,189.58	2	71,094.79	2.7536	0.5537
Difference between *A* punching and *C*, *D* and *E* punching	1,399.68	1	1,399.68	0.7897	0.6771
Interaction, bakers *C*, *D* and *E* vs. *A* and *C*, *D* and *E* punching	6,605.34	2	3,302.67	1.2190	0.5537
Random error	84,819.40	294	288.50		
Machine Moulding					
Difference between bakers *C*, *D* and *E*	12,985.89	2	6,492.94	1.5791	0.5537
Difference between *A* punching and *C*, *D* and *E* punching	509.60	1	509.60	0.3067	0.6771
Interaction, bakers *C*, *D* and *E* vs. *A* and *C*, *D* and *E* punching	16,698.31	2	8,349.16	1.7048	0.5537
Random error	81,114.60	294	275.90		
Total	475,770.68	599			

TABLE LX

DIFFERENCES BETWEEN HAND AND MACHINE RESULTS

	Mean loaf volume in cc., hand-machine results		
	Baker *C*	Baker *D*	Baker *E*
A punching	18.0	55.7	17.1
C, *D* or *E* punching	23.8	46.3	15.5

values for baker *D* are in fact in ascending order according to the amount of manipulation that he performed on the dough.

A punched, *D* moulded with machine	571.0 cc.
D punched, *D* moulded with machine	589.3 cc.
A punched, *D* moulded by hand	626.7 cc.
D punched, *D* moulded by hand	635.6 cc.

In Table LXI, the results of a separate variance analysis for the data of *C*, *D*, *E* respectively are given. In each instance, the difference between *A* and these operators conducting the punching is highly significant, and, with the exception of baker *D*, the interaction of the two operators punching with hand and machine moulding is not significant.

TABLE LXI

EFFECT OF PUNCHING VERSUS MOULDING IN PRODUCING VARIABILITY BETWEEN BAKERS
VARIANCE ANALYSIS OF LOAF VOLUME DATA; HAND AND MACHINE RESULTS COMBINED, FOR BAKERS *C*, *D* AND *E* RESPECTIVELY

	Sum of squares	Degrees of freedom	Mean squares	*Z*	5% Pt.
Difference between bakers *C*,*D* and *E*	119,731.61	2	59,865.80		
Baker C					
Difference between *A* and *C* punching	7,800.00	1	7,800.00	1.9890	0.6854
Difference between hand and machine moulding	21,861.40	1	21,861.40	2.5043	0.6854
Interaction, *A* and *C* punching × hand and machine moulding	429.25	1	429.25	0.5390	0.6854
Difference between pairs	35,865.25	98	365.97	0.4592	0.1670
Random error within pairs	14,312.85	98	146.05		
Baker D					
Difference between *A* and *D* punching	9,234.40	1	9,234.40	1.8079	0.6854
Difference between hand and machine moulding	129,795.12	1	129,795.12	3.1294	0.6854
Interaction *A* and *D* punching × hand and machine moulding	1,118.65	1	1,118.65	0.7525	0.6854
Difference between pairs	41,061.29	98	418.99	0.2614	0.1670
Random error within pairs	24,341.73	98	248.38		
Baker E					
Difference between *A* and *E* punching	6,601.01	1	6,601.01	1.8613	0.6854
Difference between hand and machine moulding	13,235.64	1	13,235.64	2.2091	0.6854
Interaction *A* and *E* punching × hand and machine moulding	29.64	1	29.64	....	0.6854
Difference between pairs	34,716.65	98	354.25	0.3987	0.1670
Random error within pairs	15,636.21	98	159.55		
Grand total	475,770.70	599			

The most interesting comparison, however, is that between the random errors for the three bakers; baker *D* shows a much higher variability than either *C* or *E* and this is not merely a reflection of higher loaf volume. When the standard deviations are corrected for differences in mean loaf volume we have the comparison shown in Table LXII. In order to compare any two of these standard deviations we merely have to get the difference between their natural logarithms. This gives the value of *Z* which can be compared with a 5% point of 0.1670. It will be observed that the standard deviation for *D* is significantly higher than that for *C* and barely so for *E*.

TABLE LXII

	Standard deviation	Mean loaf volume, cc.	Log *e* standard deviation
Baker *C*	12.19	581.0	2.5006
Baker *D*	15.26	605.6	2.7252
Baker *E*	12.94	572.3	2.5603

The relative importance of punching and moulding personality in producing variability may be shown by comparing the ranges in mean loaf volume between the three bakers *C*, *D*, and *E* when these variables are successively eliminated. These values, calculated from Table LVIII are shown below.

TABLE LXIII

COMPARISON OF RANGES IN MEAN LOAF VOLUME BETWEEN BAKERS *C*, *D*, AND *E* WHEN THE VARIABLES, PUNCHING AND MOULDING PERSONALITY, ARE SUCCESSIVELY ELIMINATED

	Range in mean loaf volume, cc.
C, *D* and *E* punching, *C D* and *E* moulding by hand	61.3
A punching, *C*, *D* and *E* moulding by hand	40.1, or 21.2 cc. reduction in range due to removal of punching personality
C, *D* and *E* punching and *C*, *D* and *E* moulding by machine	30.5, or 30.8 cc. reduction in range due to removal of moulding personality
A punching and *C*, *D* and *E* moulding by machine	8.7, or 52.6 cc. reduction due to removal of punching and moulding personality

These data indicate that individuality in moulding has a somewhat greater effect on the results than punching personality and that, if the influence of both variables could be removed, the differences between bakers would largely disappear.

Summarizing the data presented in this section, it is obvious that the personal equation in both punching and moulding contributes to the variability between bakers, and hence the mechanical moulder may reduce, but not eliminate the large differences in mean loaf volume which different operators secure in replicate bakings of the same flour.

V Variability in the Baking Test and Its Relation to Mean Loaf Volume

In the discussion of certain of the tables, casual mention has been made of an apparent relation between variability and loaf volume and it is of interest to examine this more closely, and particularly to compare the extent of the relation for hand versus machine moulding and for the simple versus the bromate formula. For this purpose certain of the data obtained by baker *A* on the different flours used in Series I and Series II which are reported in Tables IV and XLI may be employed. The data selected are brought together in Table LXIV. It will be observed that flours No. 4 and 9 have been

omitted and that the machine results for the second series only are included. Flour No 4 was baked only by the simple formula and furthermore starch had been added to reduce the loaf volume. Flour No. 9, which was synthesized from remnants of various experimentally milled flours, gave a much higher correlation between the pairs of loaves moulded by hand and machine than the other flours which indicated that the different aliquots going to the mixer were probably not uniform. Since the setting of the machine in Series I was not as satisfactory as that used in Series II, the hand and machine results for flours No. 5, 6 7, and 8 only have been used for a comparison of hand and machine moulding

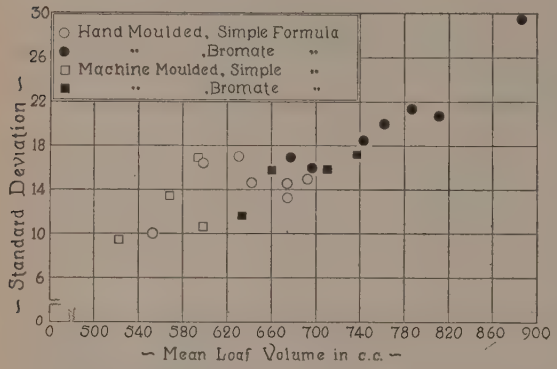

FIG. 2. *Graph showing the relation between mean loaf volume and variability.*

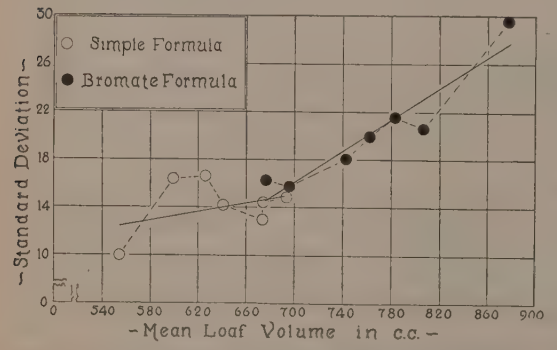

FIG. 3. *Graph showing regression of standard deviation on loaf volume for baking data obtained by the simple and bromate formula for hand moulding.*

The mean loaf volumes and standard deviations recorded in Table LXIV are presented graphically in Fig. 2 which shows that there is a decided tendency for the standard deviation of replicate bakings to increase as the mean loaf volume increases. This relationship is most marked in the results for the bromate formula. The increased variability with increasing loaf volume is not as great for the results by the simple formula, flours No. 5 and 8 moulded by hand and flour No 5 by machine being particularly out of line. With reference to flour No. 8, it will be recalled that this was a second clear flour and, when baked by the simple formula, yielded doughs of very poor handling qualities which probably accounts for the high variability obtained by hand moulding.

The extent of the relation between variability and loaf volume is indicated by the regression and correlation coefficients given in Table LXV. Considering first the results by hand and machine moulding for flours No. 5, 6, 7 and 8, it will be noted that the regression of standard deviation on loaf volume is significant for hand moulding and hardly significant for machine moulding. The difference between these two regression coefficients however is quite

TABLE LXIV

MEAN LOAF VOLUMES WITH STANDARD DEVIATIONS USED IN A STUDY OF THE RELATION BETWEEN LOAF VOLUME AND VARIABILITY

Simple formula						Bromate formula					
Hand moulded			Machine moulded			Hand moulded			Machine moulded		
Flour	Mean L. V. (x) cc.	S. D. σx cc.	Flour	Mean L. V. (y) cc.	S. D. σy cc.	Flour	Mean L. V. (x) cc.	S. D. σx cc.	Flour	Mean L. V. (y) cc.	S. D. σy cc.
6	556.6	9.92	6	523.4	9.50	5	677.8	16.39	5	634.8	11.66
8	600.0	16.31	8	568.1	13.66	8	697.8	15.88	8	660.0	15.84
5	629.4	16.76	7	594.2	16.82	1	744.1	18.09	7	712.3	15.69
7	640.6	14.43	5	597.2	10.34	7	763.3	20.00	6	737.8	17.10
2	675.0	13.23				6	785.4	21.46			
1	676.3	14.37				3	810.5	20.72			
3	693.9	14.77				2	884.4	29.68			

insignificant. For the comparison of the simple and bromate formulas, the results for hand moulding only were used. The relation for the bromate formula is highly significant as indicated by the significant positive correlation of 0.951, but is not significant for the simple formula. Fig. 3 shows this result graphically.

Considerable practical importance may be attached to the results given here as it is evident, at least when the bromate formula is used, that a flour giving a high loaf volume will probably give a correspondingly high variability. In the work of the Associate Committee on Grain Research in Western Canada it has been customary to require duplicate bakings to agree within 20 cc. Where the loaf volumes fail to agree within this limit the baking is repeated and the results averaged. Disregarding for the moment the justification of this figure for any one mean loaf volume it is evidently not the correct figure for all loaf volumes. Thus when a flour is being baked in duplicate by the simple and bromate formula the loaves baked by the latter method should not be expected to check as closely as the former if the flour shows a positive response to bromate resulting in larger loaves.

Referring to the correct value to take as the maximum spread to be allowed between duplicate bakes, this would seem to depend—first, on the arbitrary adoption of a probability value, and secondly, on the standard deviation which would be obtained in replicate bakings of the flour in question. With a standard deviation of 16 cc. for any given flour and baking method, a population of differences between duplicate bakes made within the same day would be distributed around zero as mean with a standard deviation of $16\sqrt{2} = 22.63$ cc. Differences between duplicates of $2 \times 16\sqrt{2} = 45.26$ cc. would occur therefore in about 5% of the cases due to random variability. Differences are not to be considered significant unless they are greater than that to be expected in 5% of the cases so that with the flour in question one would not be justified in discarding duplicate bakes unless the difference between them was at least 45 cc. The present limit of 20 cc. seems on this basis to be much too low.

TABLE LXV

CORRELATION AND REGRESSION COEFFICIENTS SHOWING THE RELATION BETWEEN STANDARD DEVIATION AND LOAF VOLUME

A. HAND VS. MACHINE MOULDING. (RESULTS FOR FLOURS NO. 5, 6, 7, AND 8 BY SIMPLE AND BROMATE FORMULAS)

Hand moulded				Machine moulded				Hand vs. machine		
Regression coefficient	Correlation coefficient	Significance		Regression coefficient	Correlation coefficient	Significance		Difference between regression coefficients	Significance of difference	
b_x	r	t	5% pt.	b_y	r	t	5% pt.	$b_x - b_y$	t	5% pt.
0.0398	0.8930	4.86	2.45	0.0283	0.683	2.29	2.45	0.0115	0.78	2.18

B. SIMPLE VS. BROMATE FORMULA. (RESULTS FOR FLOURS NO. 1, 2, 3, 5, 6, 7 AND 8 BY HAND MOULDING)

Simple formula				Bromate formula				Simple vs. bromate		
Regression coefficient	Correlation coefficient	Significance		Regression coefficient	Correlation coefficient	Significance		Difference between regression coefficients	Significance of difference	
b_s	r	t	5% pt.	b_B	r	t	5% pt.	$b_B - b_s$	t	5% pt.
0.0190	0.399	0.97	2.57	0.0634	0.951	6.86	2.57	0.0444	6.12	2.23

NOTE:—*x, hand moulded; y, machine moulded; s, simple formula; B, bromate formula.*

The frequency of the occurrence of a given difference between duplicate bakes will vary with the standard deviation and it has been observed that the latter varies with mean loaf volume. Consequently it is possible to set up a rough table giving mean loaf volumes, standard deviations, and the reasonable limits within which duplicate bakings should be expected to check. Taking the approximate standard deviations for different loaf volumes from Fig. 2, the following results are secured.

TABLE LXVI

MEAN LOAF VOLUMES, STANDARD DEVIATIONS AND REASONABLE LIMITS WITHIN WHICH DUPLICATE BAKINGS SHOULD CHECK

Mean loaf volume cc.	Standard deviation cc.	Reasonable limit for differences between duplicates S. D. $\times 2\sqrt{2}$ cc.
500	12	33.9
550	13	36.8
600	14	39.6
650	15	42.4
700	16	45.2
750	17	48.1
800	18	50.9
850	19	53.7
900	20	56.6

In baking only two loaves of one flour the best available estimate of the true mean is the mean of the two determinations. If the mean is 800 cc. the duplicate bakings should check within 51 cc. and if the mean is 500 cc. the duplicates should check within 34 cc. By adopting such a policy one would at least be certain that, on the whole, results would not be discarded more frequently from flours yielding high loaf volume than from flours yielding low loaf volume.

This study of variability makes possible also an estimate of the accuracy with which results can be obtained when only two loaves are baked. As an example let us assume that duplicate baking tests are made on a series of 30 flours and that the standard deviation of the experiment is 14. This standard error for the entire experiment would be determined by a variance analysis or some similar method. The standard error of the mean for any one flour is $\frac{14}{\sqrt{2}}$ and the standard error of the difference between the means for any two flours will be $\frac{\sqrt{2} \times 14}{\sqrt{2}} = 14$. In order to be reasonably certain that any two flours actually differ in loaf volume, this implies that the difference between the means of duplicate bakes must be 28 cc. or greater. Greater accuracy can be obtained by baking more loaves of each flour and in order that a given difference shall be significant we can work backwards to the number of loaves that should be baked. In order to be able to say that a difference of 20 cc. between the mean loaf volumes of two flours would only occur by chance in 5% of the cases, that is, that a difference of 20 cc. would represent a significant difference in volume we would have:

$$20 = \frac{2\sqrt{2}\ \sigma}{\sqrt{n}} \quad \text{or } n = \frac{8\sigma^2}{(20)^2}$$

where σ is the standard error of entire experiment, and n, the number of replicate bakings required. In the above example where $\sigma = 14$, $n = 4$ approximately.

The generalized formula for n is $\frac{8\sigma^2}{D^2}$ where D is the minimum significant difference selected and this can be used to determine n for any given standard deviation and minimum significant difference. Taking $D = 20$, it is interesting to compare the number of loaves that must be baked with different standard deviations.

Solving $n = \frac{8\sigma^2}{D^2}$ for different values of σ from 10 to 24 we have:

TABLE LXVII

VALUES OF n FOR DIFFERENT VALUES OF σ

Standard deviation	10	14	16	18	20	22	24
n	2.00	3.92	5.12	6.48	8.00	9.68	11.52
Nearest integer to n	2	4	5	6	8	10	12

The nearest integers to the calculated values of n furnish a rough guide to the number of loaves that should be baked for given standard deviations. Reference to Fig. 2 shows that standard deviations varying from 10 to 24 may easily be obtained and with high variability it is increasingly important that a sufficient number of loaves be baked in order to reach a given degree of accuracy. This result serves also to emphasize the necessity of exercising as much control as possible over the experiment in order to reduce the standard error.

Discussion

One would gather from statements and opinions in the literature that the introduction of mechanical moulding might be expected to overcome most of the variability encountered in the experimental baking test. The results of the studies reported here involving 4040 individual baking tests, show quite clearly that the manual manipulation of the doughs during moulding is not a factor of such great importance as has been commonly supposed by workers in this field.

Our data show that hand moulding is at least not a very important factor in contributing to the variability of replicate bakings of the same flour. The results based on 492 pairs of loaves obtained in the second series by an experienced operator showed a significant but slight reduction in variability for machine moulding, the values, expressed as coefficients of variability, being 2.88% and 2.57% for hand and machine moulding respectively. It would be expected that inexperienced bakers would mould by hand less uniformly than an experienced operator and hence that the machine would show up to better advantage when the baking was done by less experienced operators. The results, however, do not conform to this idea since no significant reduction in the random variability of replicates was effected by machine moulding in the instance of three inexperienced bakers when the variance was corrected for the differences in mean loaf volume. Furthermore, machine moulding did not reduce the difference between the loaf volumes obtained by one operator on different days—in fact the range between the means for the machine results was greater than for hand moulding—nor remove the trends which occurred within days. Factors other than "changing disposition" in hand moulding must be largely responsible for the variations in loaf volume which occur between replicates, between days, and between baking intervals within days.

The depression in loaf volume, lack of boldness, coarser texture, and duller crumb color are undesirable consequences of mechanical moulding. A lower loaf volume taken by itself is relatively unimportant, but when it is considered that both the absolute and percentage differences between the hand and machine results increase with increasing loaf volume, machine moulding obviously tends to reduce the differences between flours and between the results obtained by different baking formulas. In judging bread, it has been our experience that it is more difficult to distinguish between relative degrees of coarseness in texture than between fine silky textures. The judging of crumb color, which is at best a difficult task, is complicated when one has "dullness" occurring with various shades of yellow, which are shown by loaves baked from unbleached

experimentally milled flours. However, one could probably soon become accustomed to scoring machine-moulded loaves, and, in general, our data indicate that hand and machine moulding give essentially the same relative results on different flours.

While variations in the manual manipulation of doughs by any one operator are apparently relatively unimportant in relation to the sum total effect of other factors causing variability between replicates, our data indicate that "moulding personality" is a factor in contributing to the differences between bakers. In the comparison of punching and moulding as factors producing variability between bakers, operators of varying experience were purposely used and the range between their results is probably greater than would be obtained in the instance of experienced bakers. The results show quite conclusively that the personal element in punching, although apparently secondary to moulding, is an important factor contributing to the variability in loaf volume between bakers. The introduction of mechanical moulding may be expected to reduce but not eliminate the large differences in mean loaf volume which different operators working in the same or different laboratories secure in replicate bakings of the same flour. In fact, in the first series of experiments machine moulding gave no reduction in the variability between bakers. This may have been due to poor adjustment of the machine. In the second series the adjustment was selected after an extensive series of trials on different flours and it is felt that the setting selected was very close to the optimum for the various doughs considered as a whole, although there is no evidence that the machine yielded perfect uniformity in its portion of the experiment.

Aside from the question of mechanical moulding the data obtained by an experienced baker for hand moulding are of considerable interest. Ranges in loaf volume from 35 to 120 cc. obtained in 50 replicate bakings of a given flour within one day by an experienced baker under presumably standard conditions, are worthy of careful consideration. The increase in variability of replicate bakes with increasing mean loaf volume is of particular interest in relation to the reliability of the mean value of duplicate bakings for flours or methods yielding loaf volumes of different magnitude.

An equally disturbing result is the variability between consecutive days obtained by one operator, using the same equipment and basing the daily means on the results of 50 replicate bakes of the same flour. This variability is apparently not due to changing disposition in moulding since the use of the mechanical moulder did not decrease the range in mean loaf volume.

The present study does not throw any light on the causal factors involved in these variations. However, it will be recalled that significant positive correlations were obtained between the pairs of hand- and machine-moulded loaves indicating that a portion of the variability was systematic. This cannot be attributed to constant localized differences in the baking cabinet or oven, both of which were equipped with rotary shelves, since the trends for the baking intervals on the five days were not similar, with the exception of the last loaves baked. These doughs, however, occupied positions in the cabinet where doughs earlier in the day's bake had been placed, and for which

there was no corresponding trend. Variability in mixing would account for the correlations obtained and, in view of this possibility, a study of mixing is being undertaken.

From the results presented it is obvious that much detailed work remains to be done in elucidating and eliminating the factors responsible for variability before the accuracy of the experimental baking test can be brought within desirable limits.

Note:—On page 422 of this paper, line 20 "Werner (16)" should read "Werner (17)," and on page 427 the last sentence in the paragraph under Table I should read, "Setting Cc was selected as giving results most comparable with hand moulding and this adjustment was employed in all subsequent moulder trials of Series A".

Acknowledgments

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The authors wish to thank Mr. L. D. Sibbitt, Mr. Alan MacLeod, and Mr. W. S. Rowland, who acted as operators in obtaining part of the experimental data for a study of the variance between bakers. Their thanks are also due to Mr. A. W. Alcock, Chief Chemist, Western Canada Flour Mills Company, Limited, Winnipeg, for his kindness in selecting and supplying some of the flours used, and also for valuable assistance rendered in the judging of the loaves.

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THE EFFECT OF THE ULTRA-VIOLET COMPONENT OF SUNLIGHT ON CERTAIN AQUATIC ORGANISMS III[1]

By A. Brooker Klugh[2]

Abstract

The work reported in this paper is a continuation of the experiments carried out in 1927, 1928 and 1929 at the Atlantic Biological Station. The animals experimented upon were placed in three quartz tubes which were placed in a three-compartment box, each compartment receiving only the light which passed through the filter in the front of the compartment. The animals in the first compartment received only visible radiation, those in the second compartment received both visible and ultra-violet radiation, and those in the third compartment received only ultra-violet radiation and a little of the extreme violet. Young starfishes, *Asterias vulgaris*, were found not to be affected by ultra-violet radiation. The nudibranch, *Eolis gymnota*, which occurs at depths from seven to ten metres, proved sensitive to ultra-violet. The little thin-shelled mollusc, *Yoldia sapotilla*, was found to be affected injuriously by ultra-violet, while the amphipod *Hyperia galba* which has the peculiar habit of living in the cavity of the jellyfish, *Aurelia aurita flavidula*, proved to be resistant to ultra-violet radiation.

The series of experiments carried on at the Atlantic Biological Station, St. Andrews, New Brunswick, in 1927, 1928 and 1929, on the effect of the ultra-violet component of the sun's radiation on aquatic animals were continued by the writer during the summer of 1930. The results of the experiments of 1930 constitute the present paper.

The apparatus employed was the same, with two modifications, as that used in 1927 and described in the first paper of this series (1). First, as none of the animals experimented upon required a water temperature lower than 15° C., the water which flowed through the filter-box was not brought in through the copper coil immersed in a mixture of ice and salt as had to be done in the case of the experiments in 1927. Second, a new blue-green Corning filter was placed over the ultra-violet filter to remove the extreme red which this filter passes. Spectrograms taken with a Hilger quartz spectrograph showed that this combination of the ultra-violet filter and the blue-green filter transmitted only the ultra-violet and a very small part of the extreme violet. The animals experimented upon were placed in three quartz tubes, which were placed in a three-compartment box, each compartment receiving only the light which passed through the filter in the front of the compartment. The animals in the first compartment received only visible radiation, those in the second compartment received both visible and ultra-violet radiation, and those in the third compartment ultra-violet radiation only. The box was kept so oriented that the quartz tubes were illuminated by the filtered sunlight whenever the sun was shining.

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Contribution from the laboratories of Queen's University, Kingston, Ontario, with financial assistance from the National Research Council of Canada and with the co-operation of the Biological Board of Canada.

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Experiments on Asterias vulgaris

This species is an inhabitant of the littoral and sub-littoral zones, and in the former zone the animals are exposed to direct solar radiation whenever the sun is shining while the tide is out. The young of this species are to be found in the sub-littoral zone, but not in the littoral zone, and it seemed worth while to find out whether an animal which was obviously not affected by ultra-violet radiation in the adult stage was sensitive to such radiation in its younger stages.

July 18. One young *Asterias vulgaris* placed in each compartment at 11 a m.
July 19. Bright sun with clouds. All normal.
July 20. Bright sun with clouds. All normal.
July 21. Bright sun with clouds. All normal.
July 22. Bright sun with clouds. All normal.
July 23. Bright sun all day, with a few cumulus clouds. Highest pyrheliometer (Py.) reading 1.37 gm. cal. cm^2 per minute. All normal.
July 24. Bright sun with cumulus and cirrus clouds in afternoon. Highest Py. reading 1.4. All normal.
July 25. Bright sun in morning. Cumulus clouds, thunder and rain in afternoon. All normal.
July 26. Bright sun in morning. Cumulus and cirrus clouds in afternoon. Highest Py. reading 1.40. All normal.
July 27. 9.00 a.m. All normal. Experiment discontinued as it had run long enough to show clearly that these young *Asterias vulgaris* were not affected by ultra-violet radiation.

Experiments on Eolis gymnota

This nudibranch occurs in the sea at depths of from 7 to 10 metres.

Aug. 12. 9 a.m. Three *Eolis gymnota* placed in each compartment. Bright sun in morning. Cumulus clouds from noon on.
Aug. 13. 10 a.m. All normal. Bright sun with cumulus clouds all day. 7 p.m. Those under Total filter (transmitting visible plus ultra-violet)—All dead.
Aug. 14. 10 a.m. Those under Novial filter (visible only) and ultra-violet filters alive, but the latter weak. Bright sun with cumulus and cirrus clouds all day.
Aug. 15. 8.30 a.m. N. (Novial)—All normal. U.V. (Ultra-violet)—All dead.

This experiment indicates that this species is sensitive to ultra-violet radiation. It would have been desirable to have confirmation of this by further experimentation but a sufficient number of animals of this species could not be obtained.

Experiments on Yoldia sapotilla

This little mollusc occurs at a depth of about 20 metres.

Aug. 19. 3 p.m. Three *Yoldia sapotilla* placed in each compartment. Bright sun from 3 p.m. on.

Aug. 20. 9.00 a.m. T.—All dead. N.—All normal. U.V.—All normal. Bright sun with cumulus clouds all day.
6.30 p.m. N.—All normal. U.V.—One dead.
Aug. 21. 9.30 a.m. N.—All normal. U.V.—All dead.

The results of this experiment would seem to indicate that this little thin-shelled mollusc is sensitive to ultra-violet. Here, as in the last case, it would have been desirable to carry on further experiments, but suitable animals from the same depth could not be obtained.

Experiments on Hyperia galba

This fat-bodied, large-eyed, amphipod has the peculiar habit of living in the cavity of the jellyfish, *Aurelia aurita flavidula*. From the manner in which this jellyfish floats about at, or near, the surface of the sea it is evident that it is not affected injuriously by ultra-violet radiation, though up to the present no experiments have been performed on this species owing to the difficulty of obtaining specimens small enough to live in the quartz tubes. It seemed to be of considerable interest to ascertain whether this amphipod was also comparatively immune to the effects of ulta-violet, or whether it was sensitive to ultra-violet and protected by the layer of jelly of its host which is always between it and the rays of the sun.

Aug. 22. One *Hyperia galba* placed in each compartment at 10.30 a.m. Bright sun and clear until 11.30 a.m., cirrus and cumulus clouds the rest of the day.
6.30 p.m. T.—All dead. N.—All normal. U.V.—All normal.

Aug. 23. 9.00 a.m. N.—All dead. U.V.—All dead.

Aug. 24. Three young *H. galba* placed in each compartment at 1 p.m. Cloudy all day.

Aug. 25. Bright sun with cumulus clouds all day.
7 p.m. All normal.

Aug. 26. 9.00 a.m. All normal.
Fog in morning. 12 noon. T.—One dead.
Bright sun in afternoon. 6 p.m. T.—Two dead.

Aug. 27. Bright sun with cumulus clouds all day.
12 noon. As on Aug. 26.

Aug. 28. 8 a.m. Bright sun with cumulus clouds all day. T.—Three dead.

Aug. 29. 9 a.m. N.—Two dead. U.V.—One dead.

Sept. 1. 3.30 p.m. Three young *H. galba* placed in each compartment. Hazy sun in afternoon.

Sept. 2. Fog and haze all day. 12 noon. All normal.

Sept. 3. Fog and rain in morning, haze all day. 8 p.m. T.—Two dead. U.V.—One dead.

Sept. 4. 9 a.m. T.—Three dead. U.V.—Three dead.

These experiments show that *Hyperia galba* is not especially sensitive to ultra-violet radiation.

Acknowledgment

The author wishes to acknowledge the assistance of Mr. John Stevenson in securing some of the specimens used in these experiments.

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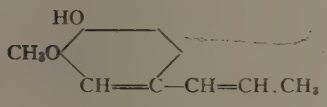
STUDIES OF POLYMERS AND POLYMERIZATION
III. THE POLYMERIZATION OF EUGENOL, SAFROLE AND THE CORRESPONDING ISO-COMPOUNDS[1]

By George Stafford Whitby[2] and Morris Katz[3]

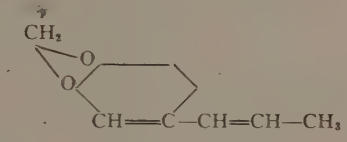
Abstract

Eugenol, isoeugenol, safrole and isosafrole when treated with stannic chloride yield polymers with molecular weights of the order of 2000, and when heated at 197° or 236° C. polymers with molecular weights of the order of 1000. The ease of polymerization of the iso-compounds, which contain a semi-benzenoid conjugated system, is markedly greater than that of the normal compounds, in which such a system is lacking. The polymers are all unsaturated. Polysafrole yields safrole when subjected to pyrolytic distillation.

Several compounds well known to be capable of yielding high polymers contain what the authors have previously (19) designated as a semi-benzenoid conjugated system; that is to say, a conjugated system involving a bond in a benzene nucleus. Examples of such compounds are styrene and indene. That a conjugated system is indeed present in such compounds is shown by measurements of such physical properties as the molecular refraction (15). Other compounds in which such a system is present are the propenyl aromatic derivatives, isoeugenol (I) and isosafrole (II), and the object of the present study was to compare the polymerizability of these compounds with that of the corresponding allyl derivatives, eugenol and safrole, in which such a system is lacking.



I



II

The presence of a conjugated system in these propenyl compounds is shown by their magnetic rotatory power (15) and is also indicated by their much higher viscosity as compared with the viscosity of the corresponding allyl compounds (17).

Hydrochloric acid and a number of other reagents (such as acid chlorides, ferric chloride, phosphorus chlorides) which are capable of yielding hydrochloric acid, have been found to convert isoeugenol and isosafrole to dimers (1, 4, 7, 8, 10-12, 16, 17). Further, formic acid has been found to convert these compounds into dimers but to be without effect on eugenol and safrole under the same conditions (6, 13). None of these reagents was observed to yield polymers higher than dimers. It seemed, however, not improbable

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that higher polymers could be obtained from isoeugenol and isosafrole by other media. Schiff (14) observed that when isosafrole was heated for several days at 320° C., it resinified, but he did not investigate the product. In the present work it was found that heat is capable of yielding polymers higher than dimers. Stannic chloride, which was used by Gerhardt (5) as long ago as 1845 to polymerize anethole, also was found to yield polymers much higher than dimers—in fact, higher than those produced by heat.

By means of heat, polymers with molecular weights of the order of 1000 were obtained, not only from isoeugenol and isosafrole but also from eugenol and safrole. The speed of polymerization was, however, markedly higher with the iso- than with the normal compounds. By means of stannic chloride still higher polymers were obtained from all four compounds, the molecular weights ranging from 1617 to 2507, but the greater ease of polymerization exhibited by the iso-compounds as compared with the normal ones was even more marked than when polymerization was brought about by heat. Full data concerning the products are given in the Experimental Part.

The greater speed of polymerization of the iso-compounds when heated is shown by the following illustrative data.

TABLE I

COMPARATIVE RATES OF POLYMERIZATION OF NORMAL AND ISO-COMPOUNDS

Temp. ° C.	Time, days	Percentage polymerized			
		Eugenol	Isoeugenol	Safrole	Isosafrole
197	6	34.0	72.9		
197	16	47.6	87.6		
197	29			29.7	47.7
238	1	24.15	47.2		
	2.125	41.6	89.0	12.9	44.4

As was found (19) in the case of the polymerization of indene by heat, the molecular weight of the polymeric products rose in each case as the period of heating and the percentage of the material which had polymerized increased. In the case of all four compounds, when only, say, 25-30% of the material had polymerized, the molecular weight of the polymeric product was of the order of 450, whereas, when the percentage polymerized was 100 or nearly so, the molecular weight was of the order of 1000.

It was also found, as in the polymerization of indene by heat (19), that the molecular weight ultimately attained when polymerization was complete or nearly so was lower, the higher the temperature which was applied. This is shown by the data in Table II.

That the polymeric product attains a higher molecular weight at a lower polymerization temperature than at a higher is to be ascribed to the fact that large polymeric molecules undergo slow cracking on heating, as was shown in experiments on the heating of polyindenes (15), so that there is a limit to the

TABLE II

INFLUENCE OF TEMPERATURE OF POLYMERIZATION.
MOLECULAR WEIGHTS OF POLYMERIC PRODUCTS WHEN POLYMERIZATION IS COMPLETE OR NEARLY SO

	Temperature, ° C.			
	197		238	
	% Polymerization	Mol. wt.	% Polymerization	Mol. wt.
Eugenol	100	1080	94.2	955
Isoeugenol	100	987	100	842
Safrole	82.3	960	82.6	862
Isosafrole	89.8	1016	93.4	790

size of polymeric molecules which can exist at a given temperature. The occurrence of such cracking in the case of the present series of polymers was indicated by the observation that on heating isoeugenol at 238° C. for four days, when polymerization had completed itself, the molecular weight of the product was 842, whereas, on continuing the heating for a further period of four days, it had fallen to 783.

When treated with bromine the heat polymers from all four compounds showed both addition and substitution of bromine. An attempt was made to ascertain the degree of unsaturation of the polymers by the use of McIlhiney's method (9) for distinguishing between added and substituted bromine. The bromine added was found in all cases to be in excess of one atom per mole but to be in no case as high as two atoms per mole. The highest figure was 1.79 atoms per mole. Unsaturated compounds of high molecular weight frequently show sluggishness in their addition reactions and it would seem probable that in the limit the bromine absorption of the polymers of eugenol, isoeugenol, safrole and isosafrole would be two atoms of bromine per mole and that their molecules contain one double bond. This suggests that the mechanism by which the polymers are formed is in the main similar to that proposed for the formation of polyindenes (19) and polystyrenes (18).

When added to undiluted isoeugenol and isosafrole, stannic chloride produced a violent reaction and led to charring, whereas with eugenol and safrole it

TABLE III

POLYMERIZATION BY STANNIC CHLORIDE

	Conditions of treatment		% Polymerization	Mol. wt. of product
	Diluent	Time		
Isoeugenol	Chloroform	18 hr.	55	2059
Isosafrole	Chloroform	Several days	64	2507
Eugenol	None	3 mo.	37	1808
Safrole	None	3 mo.	37	1671

reacted only very slowly. Further, it gave polymeric products of higher molecular weight from the iso- than from the normal compounds. The difference in behavior of the iso- and normal compounds when treated with stannic chloride is shown by the results in Table III.

In view of the greater ease with which the iso-compounds undergo polymerization and the fact that certain reagents (*e.g.*, caustic alkalies and metallic sodium) are known to be capable of converting the normal to the iso-compounds, consideration was given to the possibility that the production of polymers from eugenol and safrole might depend on these substances first isomerizing to the corresponding iso-compounds. The evidence obtained on this point, however, seems to show that the polymers in question are derived directly from the normal compounds and are veritable polymers of the latter. A sample of the polymer obtained from safrole by means of stannic chloride was subjected to pyrolytic distillation under reduced pressure and was found to yield safrole, not isosafrole. The safrole was identified by its boiling point and by the fact that, in contrast to isosafrole, it failed to yield a picrate.

Experimental

The ethers used were purified by fractional distillation, the final distillation being carried out under reduced pressure. The boiling points at 2-4 mm. were as follows:— eugenol, 87-89; isoeugenol, 95-97.5; safrole, 69-72; isosafrole, 89-91° C.

Polymerization by Heat

Quantities of about 12 gm. each of the ethers were kept for various periods of time in sealed glass tubes at 197 and 238° C. by suspension in the vapor of liquids boiling at these temperatures. The contents of the tubes changed in character as polymerization proceeded as follows. When 15-20% of polymerized material was present, the viscosity had clearly increased and the color deepened—to yellow, in the case of safrole and isosafrole; to orange, in the case of eugenol and isoeugenol. When the amount of polymerization had reached 40-50%, the contents of the tube would, on cooling, set to a gel in the case of eugenol and isoeugenol, and to a viscous oil which flowed with difficulty, in the case of safrole and isosafrole. At 80-90% polymerization the products from eugenol and isoeugenol were red, clear resins; from safrole and isosafrole, deep orange to light red gels.

At the conclusion of the various heating periods, unchanged monomer was removed by distillation at 2-4 mm. from a tared flask; the undistilled, polymeric products were weighed and dissolved in benzene or chloroform, and the solution was then poured drop by drop into three volumes of petrolic ether (b.p. 40-60° C.), the liquid being stirred mechanically meanwhile. The amorphous powder thus obtained was subjected to three or four further precipitations by petrolic ether, the solvent being alternately benzene and chloroform. The products were pale yellow or light brown powders. On evaporating the combined filtrates to 50 cc., in no case did any further separation take place. The products were very soluble in benzene, toluene, chloroform, carbon tetrachloride

and acetone; fairly soluble in ether and alcohol; insoluble in petrolic ether. Solutions of the polymers were not viscous and not apparently colloidal.

As purified by the series of precipitations mentioned, the products had a higher molecular weight than in the crude condition immediately following the removal by distillation of unchanged monomer. This was presumably due to the fact that the crude products contained a certain amount of monomer which the distillation had failed to remove. The following data for a typical case illustrate this point. They refer to the polymeric product obtained by heating eugenol for eight days at 238° C. (a) Crude polymer (brittle, red resin), mol. wt.: 549, 556. (b) Reprecipitated polymer (amorphous powder), mol. wt.: 975, 933.

The following table shows the progress of polymerization and the molecular weights (determined in duplicate) of the reprecipitated polymers.

TABLE IV

POLYMERIZATION BY HEAT

Time days	Polymerization %	Mol. wt. of polymer 1	2	Av.	Polymerization %	Mol. wt. of polymer 1	2	Av.
At 197° C.								
	Isoeugenol				Eugenol			
2	27.3	438	449	444				
6	72.9	713	690	702	34.0	461	453	457
16	87.6	825	844	835	47.6	637	648	642
29	100.0	979	994	987	61.0	909	847	878
61		872	893	883	100.0	1108	1052	1080
	Isosafrole				Safrole			
16	30.8	482	476	479				
29	47.7	706	690	698	29.7	431	445	438
35					43.7	628	605	617
61	89.8	1037	995	1016	82.3	951	970	961
At 238° C.								
	Isoeugenol				Eugenol			
1	47.2	496	480	488	24.15	427	420	424
2.125	89.0	604	615	610	41.6	585	596	591
4	100.0	851	832	842	76.3	725	743	734
8	100.0	769	797	783	94.2	973	933	955
	Isosafrole				Safrole			
1	25.8	457	443	450				
2.125	44.4	648	637	643	12.9	446	431	439
4	76.5	713	736	725	36.2	558	573	566
8	93.4	762	818	790	82.6	874	850	862

The last polymer in each series was analyzed, with the following results:—
Polyisoeugenol. Calcd. for $(C_{10}H_{12}O_2)_x$: C, 73.05; H, 7.30. Found:— 29 days at 197° C.: C, 73.15; H, 7.06; 8 days at 238° C.: C, 72.55; H, 7.04%.
Polyeugenol. Found:— 61 days at 197° C.; C, 73.10; H, 7.24; 8 days at 238° C.: C, 73.15; H, 7.18%.
Polyisosafrole. Calcd. for $(C_{10}H_{10}O_2)_x$: C, 74.03; H, 6.16. Found:— 61 days at 197° C.: C, 73.90; H, 6.05; 8 days at 238° C.: C, 74.20; H, 6.37%.
Polysafrole. Found:— 61 days at 197° C.: C, 74.20; H, 6.20; 8 days at 238° C.: C, 73.81; H, 6.24%.

Bromine Absorption of the Heat Polymers

Preliminary experiments in which samples of the polymers were treated with Hubl's solution, Hanus solution and a solution of bromine in chloroform, indicated that substitution as well as addition occurred. The method of McIlhiney for distinguishing between added and substituted bromine was therefore applied. Weighed samples of a number of the polymeric products in

TABLE V
BROMINE ABSORPTION OF THE HEAT POLYMERS

Wt. of sample gm.	Mean mol. wt.	Excess bromine, cc. 0.1 *N* thiosulphate	Substituted bromine, cc. 0.1 *N* thiosulphate	Bromine added per mole, atoms
Polyisoeugenol				
0.4220	444	20.5	38.2	1.56
0.4475	610	22.7	40.6	1.40
0.4129	835	25.1	42.0	1.31
0.6181	987	23.3	20.8	1.52
Polyeugenol				
0.4476	457	27.9	28.4	1.77
0.4891	642	30.0	31.2	1.63
0.4696	878	30.2	36.4	1.31
0.5753	955	34.1	31.0	1.41
Polyisosafrole				
0.3335	479	40.1	22.0	1.64
0.4130	643	38.4	24.8	1.62
0.5757	698	33.9	26.6	1.58
0.5641	1016	44.0	23.2	1.15
Polysafrole				
0.4025	438	35.8	21.4	1.78
0.4529	617	40.3	20.2	1.79
0.5664	862	43.7	20.8	1.38
0.5680	961	42.5	21.4	1.64

chloroform solution were left to stand in the dark for 24 hr. after the addition of 40.0 cc. of an 0.184 *N* solution of bromine in chloroform. Potassium iodide was added and excess bromine was titrated with 0.1 *N* thiosulphate solution. Potassium iodate was then added at once and the bromine derived from the hydrobromic acid present was titrated. The latter represents half the bromine consumed in the substitution reaction. The results are shown in Table V.

Polymerization by Stannic Chloride

Preliminary observations (19) had shown that, whereas isoeugenol and isosafrole are quickly polymerized by anhydrous stannic chloride, eugenol and safrole are converted only slowly by this reagent, polymerization taking months to complete itself. If more than one part of stannic chloride was added to 50 parts of undiluted isoeugenol or isosafrole, reaction was so violent that the mixture charred completely. Hence these compounds were diluted before the catalyst was added and were kept at a low temperature. On addition of the catalyst to any of the compounds in question there was formed a deep red wine colored complex.

Isolation of the products was effected by the addition of petrolic ether (b.p. about 60° C.), which broke up the deeply colored complex and precipitated the higher polymers as amorphous powders or sticky masses. Stannic chloride, any unchanged monomer and any low polymers remained in the mother liquor. The precipitated polymers were purified by filtering them off, drying, dissolving in benzene and again precipitating with petrolic ether. After repeating the precipitation from benzene three or four times, the products were obtained as practically white powders. They were dried in vacuum. Lower polymers could be obtained from the mother liquor by concentration followed by the addition of petrolic ether. The polymers were soluble in benzene, toluene and chloroform; very soluble in acetone; less soluble in alcohol, ether and acetic acid, and insoluble in petrolic ether.

Isoeugenol. To a mixture of 10 gm. of isoeugenol and 10 gm. of chloroform contained in a small flask attached to a reflux condenser and cooled to 0° C. was added 1 cc. of a 20% solution of stannic chloride in chloroform. After one hour the red viscous solution was removed from the cooling bath and allowed to stand for 18 hr. at room temperature. The high polymeric product was then isolated in the manner already described. Yield, 5.5 gm. Mol. wt., 2150, 1968 (av., 2059). C, 72.60; H, 7.21%. Calcd. for $(C_{10}H_{12}O_2)_x$: 73.05, 7.30%.

Eugenol. Eugenol (50 gm.) and 1 cc. of stannic chloride was placed in a stoppered flask at 10° C. After one hour the flask was removed from the cold bath and kept at room temperature for about three months, during which time the liquid increased considerably in viscosity. Yield of high polymeric product, 18.5 gm. Mol. wt. 1738, 1877 (av., 1808). C, 72.80; H, 7.35%.

Isosafrole. To 50 gm. of isosafrole diluted with 100 gm. of chloroform was added 5 cc. of a 20% solution of stannic chloride in chloroform, the temperature being kept at 0° C. for 2 hr. The mixture was then allowed to stand at room temperature for several days and the higher polymers isolated in the way

already described. Yield, 32 gm. Mol. wt., 2420, 2593 (av., 2507). C, 74.10; H, 6.04% Calcd. for $(C_{10}H_{10}O_2)_x$: 74.03, 6.16%.

Safrole. Safrole (100 gm.) was left with 4 cc. of stannic chloride for three months at room temperature and the higher polymeric product then isolated. Yield, 37 gm. Mol. wt., 1762, 1580 (av., 1671). C, 73.70; H, 6.22%.

Pyrolytic Distillation of Polysafrole

Polysafrole (30 gm.) prepared by means of stannic chloride (*supra*) was distilled from a flask heated by a metal bath, the pressure being 6 mm. With a bath temperature of 320-365° C. there came over about 13 gm. of distillate at 70-126° C. and there remained behind a resinous mass. The distillate was fractionated at ordinary pressure. It gave a fraction (about 6 cc.) boiling at 106° C. and one (5 cc.) boiling at 230-239° C. A resinous residue remained. The fraction boiling at 230-239° C. when dissolved in alcohol and treated with an alcoholic solution of picric acid failed to yield a picrate. A sample of isosafrole treated in the same manner gave a picrate melting at 73-74° C. According to Bruni and Tornani (2) safrole and methyl eugenol do not yield picrates, whereas propenyl compounds such as isosafrole do so readily, the picrate from isosafrole melting at 73° C.

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THE DENSITY OF SULPHUR DIOXIDE[1]

By D. LeB. Cooper[2] and O. Maass[3]

Abstract

The density of sulphur dioxide has been measured by the same method as that previously described in this Journal and equations of five isothermals are given. Some evidence of adsorption influence appears in the isothermal at −7.82° C. The normal density of sulphur dioxide found is 2.9262.

The density of sulphur dioxide has been determined in the same apparatus as that used by the authors (2, 3) for the determination of the density of carbon dioxide. The method and experimental technique were the same with the exception of the determination of mass. The danger of fracture of the bulb being negligible, the tubes were conditioned in a constant-humidity box, transferred to the balance pan and weighed with the usual precautions.

Purification of Sulphur Dioxide

Sulphur dioxide, condensed from a tank of the liquid, was distilled under vacuum, and through phosphorus pentoxide until a differential manometer indicated no difference in vapor pressure between two fractions of the liquid held in a constant-temperature bath at −10° C. All the gas distilled into the storage bulbs for use was tested in this manner. The small residual pressures obtained indicated that the gas was entirely free from permanent gases.

Results

The results are shown in Tables I to V, calculations being made in the same manner as for carbon dioxide. The number of results at each individual point did not warrant calculations of the precision measures, but inspection of the various tables indicates that the maximum error is less than 0.020% for any single reading, and less for the mean. Values taken from the isothermals are judged to be correct to 0.013%.

TABLE I

Isothermal at 0.0° C.

Pressure, cm. Hg	Weight, gm.	Temperature, ° K	Volume, cc.	M'
70.978	14.8484	273.18	5443.3	65.467
72.015	15.0735	273.18	5443.3	65.501
43.422	9.0066	273.18	5443.1	64.912
43.698	9.0655	273.18	5443.1	64.924
23.787	4.9067	273.18	5442.9	64.555
23.975	4.9480	273.18	5442.9	64.585
24.555	5.0652	273.18	5442.9	64.557
23.776	4.9065	273.18	5442.9	64.583
24.279	5.0091	273.18	5442.9	64.569

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, with financial assistance from the National Research Council of Canada.
[2] *Postgraduate student, McGill University, and holder of a fellowship under the National Research Council of Canada.*
[3] *Professor of Physical Chemistry, McGill University.*

TABLE II

ISOTHERMAL AT 25.2° C.

Pressure, cm. Hg	Weight, gm.	Temperature, ° K	Volume, cc.	M'
69.621	13.2524	298.33	5444.6	65.039
68.092	12.9572	298.33	5444.6	65.019
45.768	8.6660	298.36	5444.4	64.702
46.145	8.7357	298.40	5444.4	64.699
23.961	4.5157	298.41	5444.1	64.383
23.137	4.3606	298.41	5444.1	64.389

TABLE III

ISOTHERMAL AT −7.82° C.

Pressure, cm. Hg	Weight, gm.	Temperature, ° K	Volume, cc.	M'
67.523	14.5541	265.46	5442.8	65.566
67.891	14.6435	265.36	5442.8	65.571
41.449	8.8531	265.36	5442.6	64.952
41.932	8.9598	265.36	5442.6	64.963
23.159	4.9179	265.36	5442.4	64.588
22.972	4.8790	265.36	5442.4	64.575

TABLE IV

POINTS ON ISOTHERMALS AT 50 AND 72° C.

Pressure, cm. Hg	Weight, gm.	Temperature, ° K	Volume, cc.	M'
68.916	12.0659	323.18	5445.9	64.786
68.998	12.0791	323.19	5445.9	64.780
68.074	11.1186	345.65	5447.1	64.626
68.746	11.2302	345.65	5447.1	64.635

TABLE V

MEAN VALUES OF MOLECULAR WEIGHTS CORRESPONDING TO MEAN PRESSURES. ALL ISOTHERMALS.

Temperature, ° K	Pressure, cm. Hg	M'
265.36	67.707	65.570
265.36	41.690	64.957
265.36	23.065	64.581
273.18	71.496	65.488
273.18	43.560	64.918
273.18	24.074	64.570
298.36	68.856	65.029
298.36	45.956	64.700
298.36	23.549	64.386

The isothermals are drawn in two ways as shown in Fig. 1. Those used for extrapolation for the theoretical molecular weight are shown as full lines, those for the determination of the apparent molecular weight as broken lines.

The lines may be represented by the equation $M' = aP + M_o$. For the full lines these are:

Temp. °C.	a	M_o
0.00	2.009×10^{-2}	64.064
25.28	1.418×10^{-2}	64.054

These give a mean value of 64.059 for the theoretical molecular weight, and a value of 32.059 for the atomic weight of sulphur, with an estimated error of 0.020%.

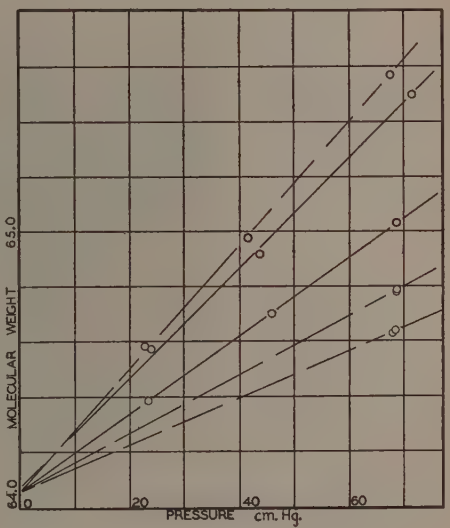

FIG. 1. *Isothermals of sulphur dioxide*

The isothermals at 50 and 72° C. were fixed by drawing a straight line through the mean molecular weight shown above, and a single set of results obtained on the isothermal near 70 cm. of mercury. The isothermal at −7.82°C. showed an indication of some adsorption on the walls of the constant-volume globe. This would give too high a molecular weight at the low pressures, and therefore this curve was not extrapolated to zero pressure for the theoretical value, but was fixed in a manner similar to the high temperature isothermals, assuming it to be a straight line.

The values for the symbols in the equations for the broken lines are:

Temp. °C.	a	M_o
−7.82	2.235×10^{-2}	64.059
50.00	1.051×10^{-2}	64.059
72.47	0.835×10^{-2}	64.059

These values agree with those obtained by Carpenter, within the limits of experimental error. The normal density of sulphur dioxide (2.9262) calculated from the above agrees with the usually accepted value, 2.9266.

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THE EFFECT OF SURFACE FILMS ON EXPLORING ELECTRODES IN GAS DISCHARGES[1]

By W. E. K. Middleton[2] and T. Alty[3]

Abstract

The presence of organic vapors in a hydrogen discharge is shown to influence greatly the current collected by an exploring electrode immersed in the discharge. It appears that the vapor molecules striking the collector may remain attached to its surface thus forming an insulating layer around it and limiting the current collected. The rate of formation of this layer is obtained from the rate of decrease of current to the collector. It is shown that this rate varies very greatly with the voltage of the collector and that the time required for the current to be reduced to one-half its initial value is shortest when the collector is at the space potential.

Introduction

Much information concerning the nature of the electrical discharge through gases at low pressures has been obtained during recent years by the use of Langmuir's (1, 2) method of analysis. He studied the volt-ampere characteristics of a small auxiliary electrode, the "collector", which was immersed in the gas between the main electrodes.

This collector was connected, through a galvanometer and a potentiometer device to the anode of the discharge tube, so that the potential, V, of the collector relative to the anode can be varied and the current, i, flowing to it can be measured as a function of V.

If the collector is at a potential considerably below that of the surrounding gas only positive ions will reach it and it will become surrounded by a positive ion sheath. As its potential is increased, more and more electrons will be collected until, when the collector potential becomes greater than that of the surrounding space, the electrons will be attracted to the collector and the positive ions repelled and the current will increase very rapidly.

It has been shown (1, 2) that the ion current, i, flowing to a collector whose potential is V volts different from that of the surrounding gas, is given by the equation

$$i = IAe^{\frac{eV}{kT}} \qquad (1)$$

Here, I is the current density of the ions in the ionized gas; A, the area of the collector; k, Boltzmann's gas constant per molecule $= 1.37 \times 10^{-16}$ and T, the absolute temperature corresponding to the velocity distribution of the ions. It therefore appears that

$$\log i = K + \frac{eV}{kT} \qquad (2)$$

Formula (2) no longer applies when the ions are attracted to the collector. The current flowing when the ions are attracted depends on the shape of the

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Contribution from the Physics Laboratory, University of Saskatchewan, Saskatoon, Canada.

[2] *Graduate student and holder of a bursary under the National Research Council of Canada, 1928-1929.*

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collector. As thin wires were used in the following work, only this type of collector will be considered here. For a wire of small radius attracting ions from a gas in which I is small, Langmuir shows that the collector current is given by the expression

$$i^2 = \frac{4A^2 I^2}{\pi}\left(\frac{Ve}{kT} + 1\right).$$

Considering then the electron current flowing to the collector, it appears that so long as the collector potential V is below the space potential, then $\log i$ will be proportional to V. When, however, the collector begins to attract electrons this relationship will be no longer valid, breaking down as seen above at the space potential. The potential at which the linear relationship between $\log i$ and V breaks down thus gives the space potential of the gas.

Further, the slope of this linear graph will be, by (2), $S = \frac{e}{kT}$, so that the electron temperature may be determined from this slope.

In applying the above theory to the examination of the discharge through hydrogen a curious disturbing effect was noted. While the results agreed well with the above theoretical predictions over almost the entire range of collector voltages, it was observed that over a comparatively small voltage range, the collector current decreased steadily with time, so that the true current corresponding to any particular voltage in this region could not be obtained. This "drifting" of the current was most probably due to the adsorption of some impurity from the gas on to the surface of the collector and could be eliminated by purifying the gas thoroughly. However, as the rate of drift appeared quite definite for each collector potential, it was considered that an examination of its cause and nature would be of interest.

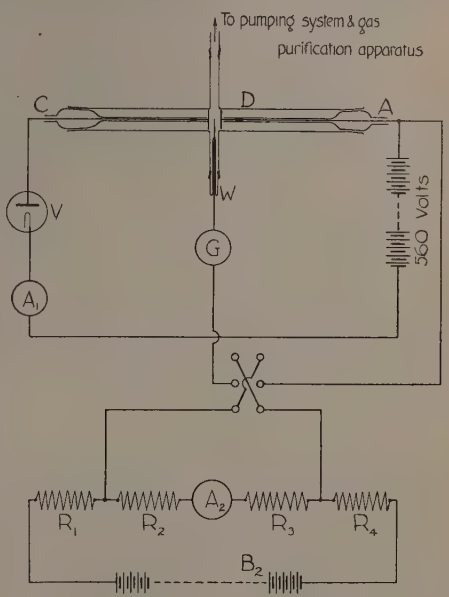

FIG. 1. *Electrical arrangements*

This paper therefore describes the result of such examination and indicates that a considerable amount of useful information may be derivable from experiments of this nature.

Experimental

The electrical arrangement employed is shown in Fig. 1. A potential difference of 560 volts was applied to the electrodes of the discharge tube D, the voltage being supplied by a battery of small accumulators. The thermionic

valve V, inserted in the circuit was used as an accurate method of controlling the discharge current. The potential between the anode A and the collector W could be varied by means of the potentiometer arrangement $R_1 - R_4$ and the battery B_2, the current to the collector being measured by means of the sensitive galvanometer G. A mercury diffusion pump backed by a Hyvac oil pump was used to exhaust the apparatus. The hydrogen used was prepared electrolytically, passed over potassium hydroxide and stored over phosphorus pentoxide before being admitted to the discharge tube. It was used in the experiments at a pressure of 1.60 mm. of mercury.

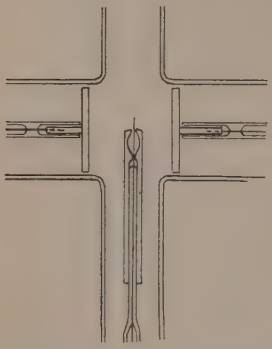

FIG. 2. *Details of experimental cell*

The details of the discharge tube itself are shown in Fig. 2. For reasons which will become apparent, it was desirable to use a tube which could easily be taken apart and thoroughly cleaned. The tube was of Pyrex glass and the electrodes of aluminium. It was outgassed by passing through it a heavy discharge from a high voltage transformer and at the same time heating it to about 400° C. in a small electric furnace which was built to fit around the tube. The ground joints projected from the ends of this furnace and were kept sufficiently cool by a blast of air directed onto them during the heating process.

The collector consisted of a short length of fine tungsten wire of diameter 0.029 mm. enclosed in a glass sheath to within a few millimetres of its free end. It was arranged so as not to touch this sheath at the point at which it emerged into the discharge.

Shortly after commencing work with this apparatus the drifting of the current already referred to was noticed.

The effect occurs only over a comparatively small range of collector voltages. Outside this range the current remains perfectly steady. Fig. 3 shows the variation of collector current with time in the region in which the variation was pronounced. It will be seen that the current decreases very rapidly to a value which is a very small fraction of the initial current. The time is measured from the time of closing the collector circuit.

It was found that the collector current could be restored to its original value by heating the collector to a red heat by electron bombardment. On repeating the experiment after such heating, the collector current had initially the same value as in the previous

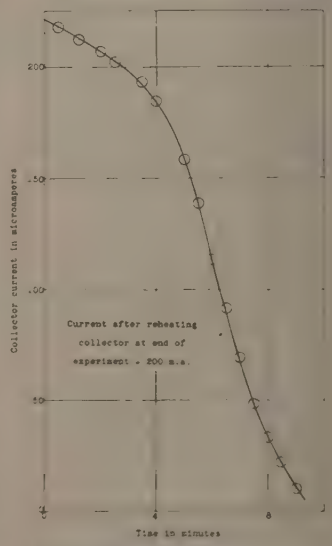

FIG. 3. *Variation of collector current with time*

experiment and decreased in the same manner. So long as the collector voltage remained constant the rate of decrease remained constant and the experiment could be repeated time after time. This experiment therefore indicates that the variation in collector current is due to the covering of the exploring electrode by a deposit which is removed by electron bombardment. When the current is not flowing to the collector, there appears to be little or no deposition on the surface of the latter.

In order to discover the nature of this deposited material, it was collected and examined spectroscopically. For this purpose, the experimental tube shown in Fig. 4-*a* was constructed.

The discharge tube, *A*, was of Pyrex glass with iron electrodes and was connected to the top of a barometer tube, *B*, which was filled with mercury. To the top of the discharge tube a capillary spectrum tube, *C*, of small volume was attached so that the spectrum of the gas in the tube could be obtained.

The apparatus was exhausted and at the same time heated thoroughly with a flame. An alternating-current discharge was passed between the iron electrodes to outgas them as completely as possible. Pure dry hydrogen was then introduced and a discharge passed between the iron electrode and the collector so as to clean the latter. The whole apparatus was then re-exhausted until no discharge would pass.

Hydrogen gas similar to that which produced a large current drift in the discharge tube used in the earlier work was introduced and the current to the collector was allowed to decrease in the ordinary way until the latter had acquired a suitable deposit. At this time the whole apparatus was thoroughly exhausted and the glass was reheated to drive off any adsorbed gases. The mercury in the barometer tube *B* was then raised to the level *D* so as to cut off the experimental cell from the rest of the apparatus and the spectrum as given by the tube *C* was photographed. This gave the mercury spectrum alone as would be expected. A strong discharge was then passed between the iron electrodes and the collector to heat up the latter and remove any deposit, and the mercury level was raised to the point *E* so that the deposit was compressed into the spectrum tube *C*. The spectrum was again photographed and showed the mercury lines as before (Fig. 4-*b*), with the addition of a series of bands, as indicated by the arrows. Comparison of this spectrum with one obtained in a carbon dioxide discharge indicates that these bands correspond closely with the bands of carbon monoxide or carbon dioxide at 4835Å and 4511Å. It thus appears that the bombardment of the deposit produced one of these gases.

As the collector current could be maintained perfectly steady without showing any sign of drifting downwards in a discharge through carbon dioxide, it appears that the deposit causing the drift cannot have been adsorbed in the form of carbon dioxide, but must have been some more complex substance which gives off this gas when bombarded. Such substance might arise from the tap grease used, if the refrigeration were inadequate, so that an experiment was performed to examine the effect of deliberately introducing a trace of grease into the discharge tube.

For this purpose the experimental cell described above (Fig. 4) was carefully cleaned and all trace of grease was removed. No taps were used, the cell being cut off from the rest of the apparatus by means of the mercury column B. The collector current, i, was then measured as a function of its potential, V, but no drift could be observed. The experiment was repeated after a trace of white vaseline had been placed inside the discharge tube. In this case the drift was tremendous, the current decreasing extremely rapidly when the collector potential was suitably adjusted. The vaseline was then removed, the apparatus thoroughly cleaned, exhausted and again filled with dry hydrogen. In this case again, the amount of the drift was minute.

It is therefore clear that the insulation of the tungsten wire is due to the steady adsorption of some volatile constituent of the vaseline. From experiments on various organic substances, it appears that some of them are adsorbed and produce a decided drift of the collector current while others are without effect. This behavior would be expected since the adsorption on tungsten will depend on the attractive forces between the adsorbed molecule and the tungsten and these will of course vary with the nature of the substance.

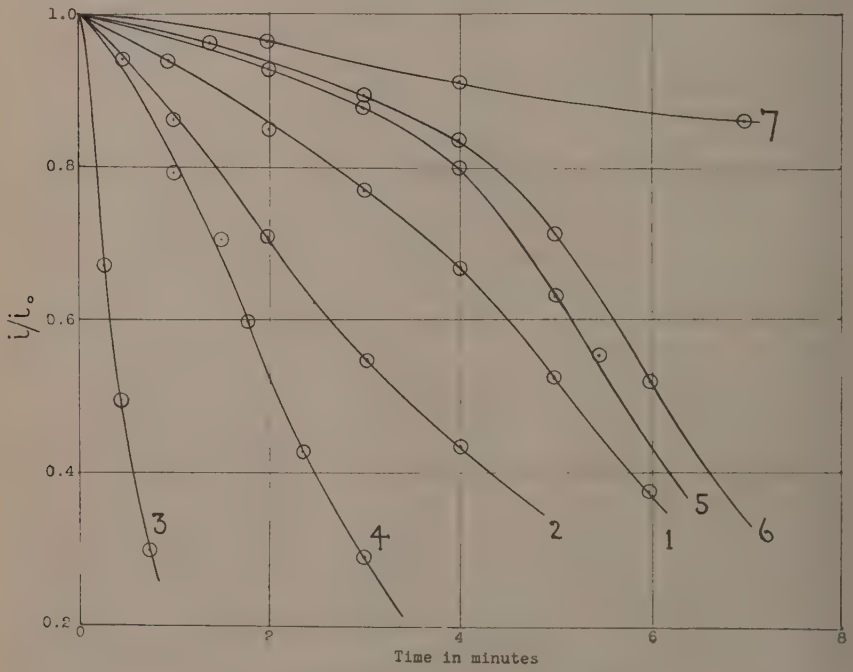

FIG. 5. *Variation of rate of drift with collector voltage*

The variation of rate of current drift with collector voltage was examined. The collector current for different voltages is plotted as a function of the time in Fig. 5 from which it will be seen that the rate of decrease of current is very sensitive to small changes in the collector voltage.

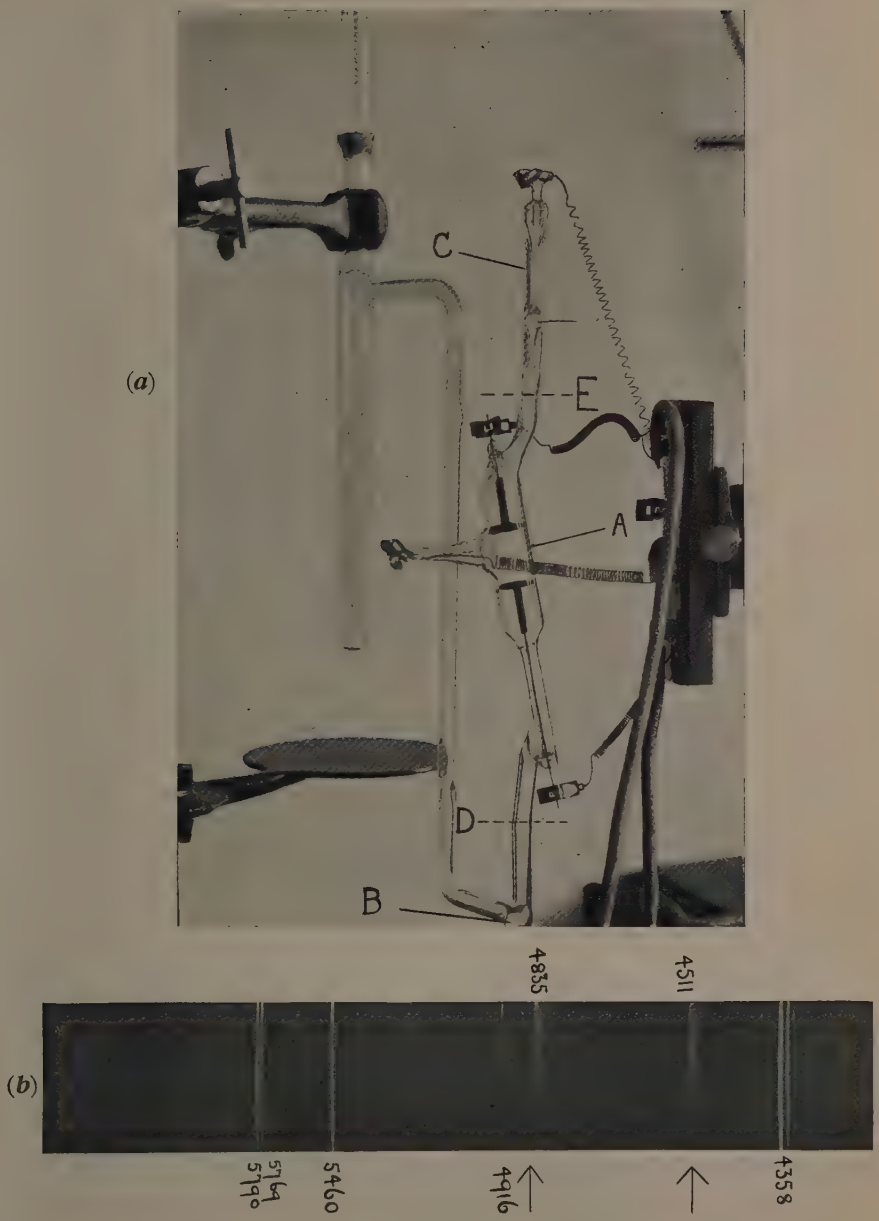

FIG. 4. *Spectrum tube and spectrogram of collected material.*

The voltages applied to the collector in the experiments whose results are shown in Fig. 5 are given in the following table:

TABLE I

VOLTAGES APPLIED TO COLLECTOR (FIG. 5)

Curve number	1	2	3	4	5	6	7
Collector voltage (relative to anode)	−18.81	−18.36	−16.08	−13.54	−11.00	−10.94	−6.15

Since the initial collector current is reproducible by heating the wire after a drift experiment, an attempt was made to obtain the usual Langmuir log $i-V$ curve by measuring the initial current for each voltage. After each current reading, the collector voltage was changed slightly, the collector heated for some seconds and the initial current corresponding to the new collector voltage measured. This method was quite successful. The electron current, i, was obtained from the total current to the collector by correcting for the positive ions collected and the log $i-V$ curve was plotted as in Fig. 6. It appears that the curve is linear up to the space potential so that the space potential and electron temperature may be obtained in the usual manner in spite of the adsorption on the collector.

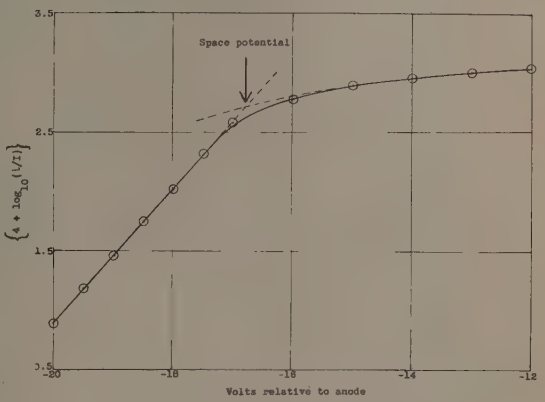

FIG. 6. *Log i-V curve in hydrogen*

It is therefore possible to compare this space potential with the potential which gives the maximum percentage rate of decrease of collector current. For this purpose, the current is measured as a function of the time for a series of progressively increasing collector voltages, the collector being heated to brightness after each change of voltage. In order to show the rate of current change as a function of the voltage, the time, T, for the current to be reduced by the drift to one-half of its original value may be obtained from these results. Values of $1/T$ are then plotted against the corresponding collector voltage. If there is no drift, $1/T$ will be zero, while the collector potential giving a maximum drift will show a maximum value of $1/T$. The curve of $1/T-V$ is shown in Fig. 7.

The curves shown in Fig. 6 and 7 were obtained under identical conditions. A comparison of these graphs shows that the current drift is a maximum at the space potential and falls off rapidly at either side of this potential. Owing to the rapid change of $1/T$ with V, the potential corresponding to $(1/T)_{max}$ may be determined fairly accurately. This might therefore be used as an alternative method of determining the space potential of the gas in the neighborhood of the collector.

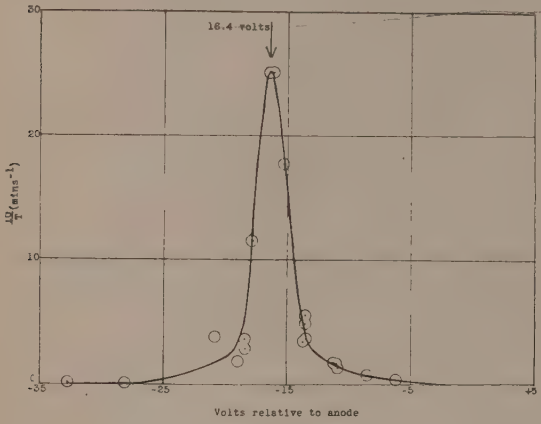

FIG. 7. $\frac{1}{T} - V$ *curve*

Conclusion

The results described above indicate that, near the space potential, the collecting electrode is partially covered by a layer of molecules of organic vapor and that this layer reduces the current flowing to the collector very considerably. In work with such collecting electrodes it is therefore essential that no such vapor should be present in the discharge.

Since the surface layer may be removed and the rate of drift varied very greatly by varying the collector potential the $1/T - V$ curves obtained for a series of different adsorbable organic vapors should give useful comparative information regarding the forces binding these different vapors to the collecting wire.

References

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2. MOTT-SMITH, H. M. and LANGMUIR, I. Phys. Rev. 28: 727-763. 1926.

A PARTICULAR CASE OF HIGH FREQUENCY ELECTRON OSCILLATIONS[1]

By. W. H. Moore[2]

Abstract

In experimenting with oscillators operating at wave-lengths of 100 cm. and less, an unusual case of oscillations was observed. With high positive grid potential and zero plate potential in a three-electrode valve, oscillations were produced at certain critical values of filament current. The frequency of oscillation was highest at the lowest filament current. An explanation of the effect is suggested.

Introduction

Several distinctly different methods have been developed for the production of short radio waves of the order of 100 cm. or so in wave-length. Oscillations in resonant circuits tuned to the desired frequency can be produced by spark coil excitation. Some types of conventional triode valve oscillatory circuits may be modified to oscillate at these very high frequencies. The magnetron, a device consisting of a diode vacuum tube upon which is superimposed a magnetic field, was originally developed for use at ordinary power frequencies, but has proved very successful in producing high frequencies of the order of 500 megacycles. A circuit arrangement using three-electrode vacuum tubes with high positive grid potentials and zero or small negative plate potentials, was found by Barkhausen and Kurz (1) in 1920 to produce oscillations at wave-lengths in the neighborhood of one metre and less.

These various methods of producing oscillations have not proved equally adaptable to the different portions of the short wave-length end of the radio spectrum. Oscillations at wave-lengths of one and one-half metres and more are most satisfactorily produced by means of the three-element vacuum tube, used in circuits which take advantage of the negative resistance characteristic of the valve to return energy, through some form of coupling, from the output to the input circuits. The magnetron oscillator covers an overlapping field of usefulness which extends down to waves of five centimetres or so in length. Barkhausen oscillators have been successfully developed for waves of from 150 cm. down to a few centimetres in length. For the shortest radio waves yet measured, between a few centimetres and a fraction of a millimetre in wave-length, spark excitation of small metallic particles has been the only successful method of production as yet devised.

This paper describes some experimental work carried out by the writer while investigating the Barkhausen type of oscillator, operating at wave-lengths between 50 and 150 cm.

[1] *Manuscript received February 28, 1931.*

Contribution from the Department of Electrical Engineering, McGill University, Montreal, Canada. A summary of this paper entitled "Centimetre Radio Waves" was presented before the Royal Society of Canada, in Montreal, May, 1930.

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Barkhausen-Kurz Oscillations

A number of workers have investigated Barkhausen oscillations since they were first discovered. The circuit generally employed for their production is that shown in Fig. 1, or some modification of it. The wave-length obtained with this type of circuit does not depend upon the external circuit, but is determined by the particular valve used and the amount of positive grid potential applied to it.

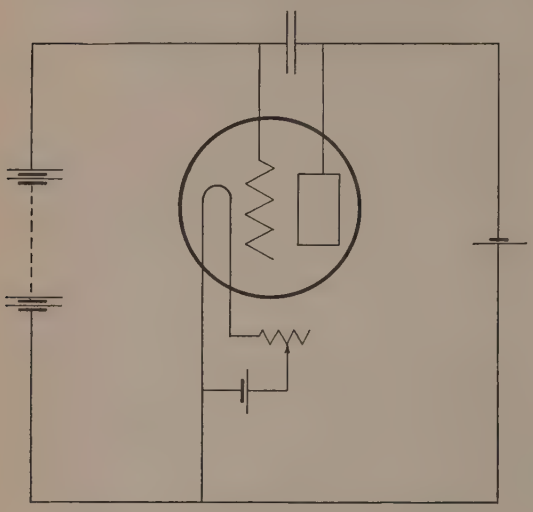

FIG. 1. *Circuit for generating Barkhausen-Kurz oscillations.*

The explanation given by Barkhausen to account for the production of oscillations under these circumstances was as follows. The electrons emitted by the filament are attracted by the positively charged grid. Some of these electrons actually strike the grid, but most of them pass through the grid interstices. They are now acted upon by the repelling force of the negative plate, towards which they are moving, and by the attractive force of the positive grid, away from which they are travelling. Both of these forces tend to retard the electrons, and will eventually reduce their velocity to zero, and then cause them to accelerate in the opposite direction. On returning through the grid spaces and moving towards the filament, the electrons will then be decelerated by the negative space charge or cloud of electrons about the filament. Thus again their velocity will be reversed, and the oscillatory motion about the grid repeated. The period of oscillation of this electron cloud will therefore be determined by the grid potential, which controls the velocity of the electrons, and by the distance between electrodes, which determines the length of the traverse. This, briefly, is a qualitative explanation of the mechanism of Barkhausen oscillations.

Apparatus

The circuit used in obtaining the curves appended to this paper is that shown in Fig. 1. A "Fotos" R type valve, of European manufacture, was used throughout these tests. It had a straight tungsten wire filament, with a helical grid and cylindrical plate mounted symmetrically about it. A number of other valves, both European and American types, were tried but most of them refused to oscillate in the Barkhausen circuit. Of those that did oscillate,

the Fotos valve was the only one which was really satisfactory in producing stable oscillations which could be reproduced readily over a considerable range of wave-lengths.

The valve was mounted in a socket in all the experiments. Choke coils consisting of about 100 turns of No. 30 copper wire wound on half-inch wooden dowel pins, were connected in plate, grid, and filament leads, but their effectiveness is somewhat doubtful. Two parallel wires, each 35 in. long, were connected to the grid and plate terminals of the valve socket, and supported at their far end by the terminals of a second valve socket, which was used only as a support for these wires. An inverted grid-leak mounting could be slid to any position along these wires, and its springs were used to carry the connections from the plate and grid choke coils to the parallel wires.

In earlier experiments a small fixed condenser was used as the sliding bridge on the plate-grid wires, but this was not connected when the curves given in this paper were taken. In later experiments the parallel wires themselves were also omitted and the grid and plate choke coils connected directly to the valve socket, oscillations still being obtained as before.

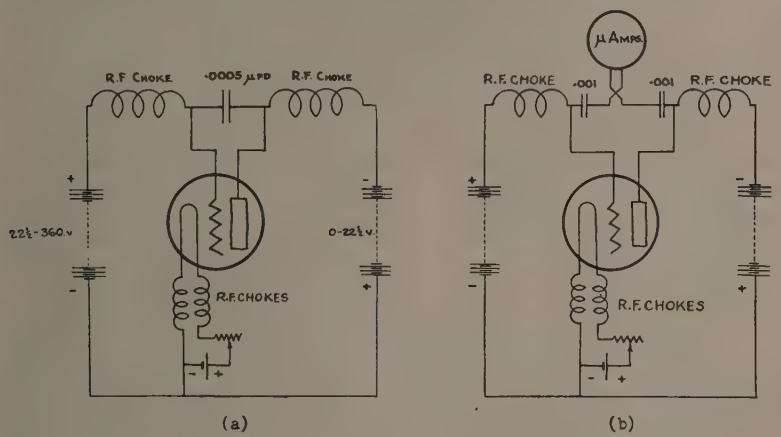

FIG. 2. *Circuits used in first experiments.*

Wave-length measurements were made by means of a Lecher wire system, and also by means of several small wave-meters calibrated against the Lecher wires. Resonance was indicated by a deflection on the plate current meter when either Lecher wires or wave-meter was coupled sufficiently closely to the valve and tuned to the wave-length of the oscillations.

When once a certain band of wave-lengths had been covered by the oscillator it was found very convenient, for further work within that band, to use a wave-meter previously calibrated from the Lecher wires, instead of using the wires directly for all wave-length determinations. The lowest range wave-meter constructed covered a range of from 45 to 70 cm. in wave-length. This particular meter consisted of a General Radio Company Type 368*a* microcondenser

with the outer two of the three rotor plates removed. The soldering lug on the stator was turned towards the rotor shaft and a globule of solder placed between the end of the lug and the metal bushing carrying the rotor. This globule of solder comprised the inductance of the wave-meter.

Several other wave-meters were constructed and calibrated by means of Lecher wires and Barkhausen and other oscillators. The wave-length range covered by these meters was from 45 cm. to over 4 metres. This provided at the top of the band covered a considerable overlap over the bottom of the range of a General Radio Company Type 358 short wave wave-meter. The overlap permitted a convenient check on the measurements made.

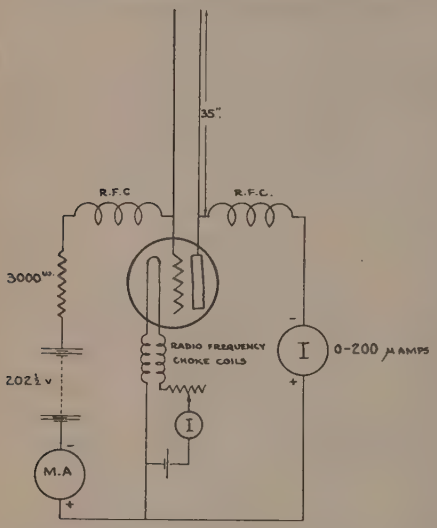

FIG. 3. *Modified circuit used in later experiments.*

This series of wave-meters is of particular interest inasmuch as it permitted a positive check to be maintained at all times on the wave-lengths produced. The fundamental wave-length of oscillation of any particular circuit could always be ascertained definitely, with no possibility of mistaking a harmonic for the fundamental. It was a common error in early work of the author and of others to mistake, for instance, a 75-cm. wave indicated on Lecher wires, for the fundamental, whereas this was actually the second or higher harmonic of a true fundamental of 150, 225, or even 300 cm. It was mainly a matter of taking the requisite amount of care to determine which was the true fundamental, of course, but it was an extremely simple matter to be in error by a factor of two or three. By utilizing a series of wave-meters covering from the shortest waves produced up to four or five metres, it was possible to determine very rapidly whether a 75-cm. wave whose presence was indicated, was a harmonic of a higher wave-length fundamental, or was itself the fundamental. The accuracy of these wave-meters is no greater than the accuracy of the Lecher wires from which they are calibrated, but their usefulness lies in the fact that they indicate but one wave-length at a time, will seldom indicate a harmonic at all unless its intensity be very great, and in any case can immediately be tuned to double or three times the wave-length to determine whether a higher wave is present or not.

Preliminary Experiments

The first tests were carried out with the circuit of Fig. 2 (a). No indications of oscillation were observed, however, the only effect produced being overheating of the valve due to excessive grid current. The valve used was a

UX-210 with its base removed. A 0-100 m.a. meter was connected in the grid circuit.

A Marconi-Osram "*R*" valve was then tested in the circuit of Fig. 2 (*b*). Two Sangamo 0.001-microfarad condensers were connected between plate and grid with a thermocouple and microammeter connected between them. Choke coils were connected in plate, grid, and filament leads as shown. The grid potential was varied from 22.5 to 300 volts positive, and the plate potential from 0 to 45 volts negative, but no current was observed in the 0-75 microampere meter connected across the thermojunction.

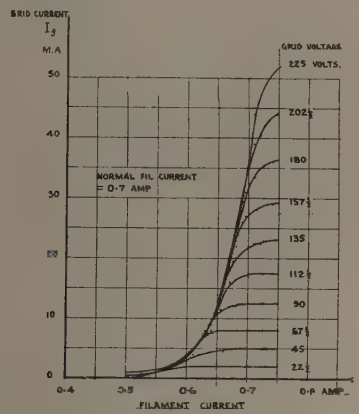

Fig. 4. $I_g - I_f$ *characteristics of Fotos straight filament R valve with* $E_p = 0$ *volts.*

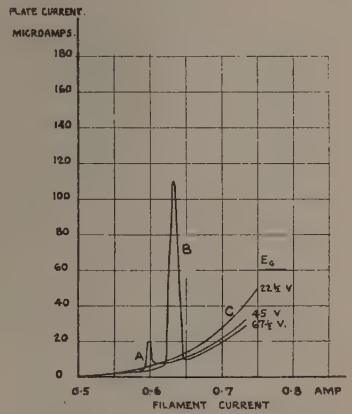

Fig. 5. $I_p - I_f$ *characteristics of Fotos R valve.* $E_p = 0$ *volts,* $\lambda = 140$ *cm. at* $E_g = +45$ *volts.* $\lambda = 130$ *cm. at* $E_g = +67.5$ *volts.*

A *UX*-210 valve was next put into this circuit. The grid current was greater than 100 m.a. at 90 volts, but no indications of oscillation were obtained on the bridge thermocouple meter in the grid-plate circuit. A 6000-ohm resistor was connected in series with the grid to limit the current at the higher voltages.

When the grid side of the parallel wire circuit was made or broken at the bridge contact, very slight deflections were obtained on the thermocouple meter. These deflections, of the order of 10 or 15 m.a., died away immediately and no constant readings could be obtained. They probably were due to transient oscillations set up in raising the grid to the potential of the battery.

The *R* valves used heretofore had helical filaments. A Fotos valve of the same type but with a straight wire filament was then tested, but with the same lack of results. It was thought that possibly the reason for the failure of the American *UX*-201*a* and *UX*-210 valves to oscillate lay in the fact that they had V-shaped filaments, and that the European *R* valves with a straight filament at the centre of a concentric cylindrical anode and grid, might be more successful in producing oscillations, since the Barkhausen action somewhat resembles the magnetron oscillation, and the magnetron requires a sym-

metrically constructed plate and filament. This appears to be the case, as the *UX*-201*a* and *UX*-210 valves could not be made to oscillate in Barkhausen circuits while the *R* valves eventually could. However, a *WD*-12 valve having cylindrical electrodes also failed to produce Barkhausen oscillations, although it was of similar construction to the *R* valves.

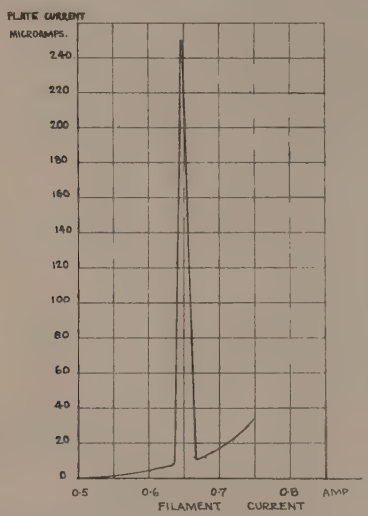

FIG. 6. *$I_p - I_f$ characteristic of Fotos R valve. $E_p = 0$ volts. $E_g = +90$ volts. $\lambda = 115.6$ cm.*

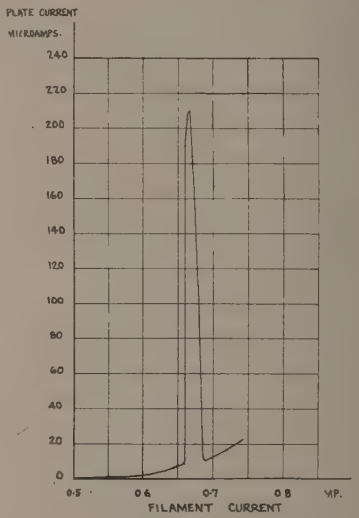

FIG. 7. *$I_p - I_f$ characteristic of Fotos R valve. $E_p = 0$ volts. $E_g = +112.5$ volts. $\lambda = 107$ cm.*

In all of the Barkhausen circuits tested so far, no meter was placed in the plate circuit, as it was expected that a deflection of the grid meter would occur to indicate when the circuit began to oscillate. It was now found that this was not so, any change in grid current occurring upon commencement of oscillations being quite too small to be observable. A 0-1 m.a. meter was inserted in the plate circuit of the Fotos *R* valve in a Barkhausen circuit and immediately it was found that oscillations were being obtained, the wavemeter producing a sharp deflection in this meter when tuned to resonance.

The wave-length measured on Lecher wires was 81.8 cm. This was carefully checked to make sure that it was the fundamental and not the second harmonic of a 163.6-cm. wave. No deflection whatever could be obtained with wavemeters tuned to multiples of 81.8 cm., so this was certainly the fundamental. In this particular case the bridge on the grid plate wires was placed about 50 cm. from the valve socket, and the following readings were recorded:

I_p	I_g	I_f	E_p	E_g	I_o
0.6 m.a.	35.0 m.a.	0.68 amp.	0 volts	+112.5 volts	0 m.a.

I_o was the reading of the thermogalvanometer in the grid-plate wires bridge.

The Fotos straight filament *R* valve was then set up in the Barkhausen oscillator. The grid voltage was varied from 22½ to 225 volts and the plate voltage left at zero. Values of grid and plate current were read over a range of variation of filament current, and graphs of these quantities plotted for each value of plate voltage. (See Fig. 4-13.)

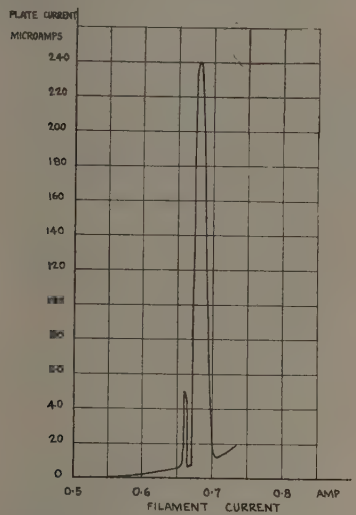

FIG. 8. *$I_p - I_f$ characteristic of Fotos R Valve. $E_p =$ 0 volts. $E_g = +135$ volts. $\lambda = 85$ cm. at lower peak and 100 cm. at higher peak.*

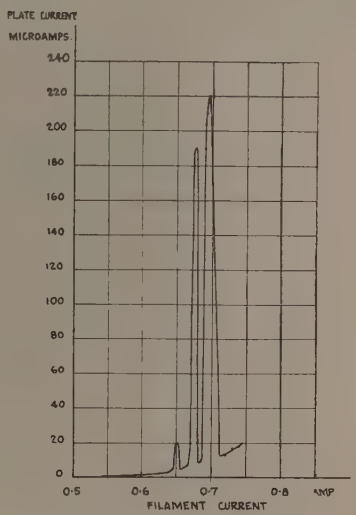

FIG. 9. *$I_p - I_f$ characteristic of Fotos R valve. $E_p =$ 0 volts. $E_g = 157.5$ volts. $\lambda = 69$, 82 and 97 cm. at lowest, middle and highest peaks, respectively.*

Peculiarities Observed

A number of very striking facts immediately stand out from the curves of Fig. 5-13. It will be observed that in each case oscillations are indicated by a sharp peak in the plate-current curve, but that no such peak is produced in the corresponding grid-current curve. The grid-current curves (Fig. 4), are, as might be expected, of the same form as normal plate-current curves taken with positive plate voltages. They do not all coincide at the lowest filament currents because the grid-current milliammeter used could not be read accurately at the bottom of its range. Also the curves were taken on different days, and the valve characteristics were found to vary somewhat from day to day. It is possible that there were slight kinks in the grid-current curves during oscillation which it was beyond the accuracy of the meter to record. The plate current was always very small, a microammeter being required to register it.

Fig. 5 shows the plate current-filament current characteristics for several positive grid voltages. As the grid voltage is increased the plate current decreases (except at "resonance" values), as might be expected, since the higher the potential of the grid for a given filament emission the more electrons will

be attracted to it and the fewer will reach the plate. The plate current did not reach a saturation value for any grid voltage or filament current used.

When the grid voltage was $22\frac{1}{2}$ no oscillations were obtained (curve C, Fig. 5). When the voltage was increased to 45, curve A of Fig. 5 was obtained, showing a sudden increase of plate current at a filament current of 0.6 ampere. It was found that the hump in the curve indicated the presence of oscillations of wave-length 140 cm., but that at values of filament current on either side of the hump no oscillations were produced. Thus in this particular case the Barkhausen oscillations occurred only within the extremely narrow range of filament current of about 15 m.a. The middle of this range was at 0.6 ampere, which is considerably below the normal filament current (0.7 ampere) for this valve. Similar graphs were obtained for each of the other cases and are shown in the other figures.

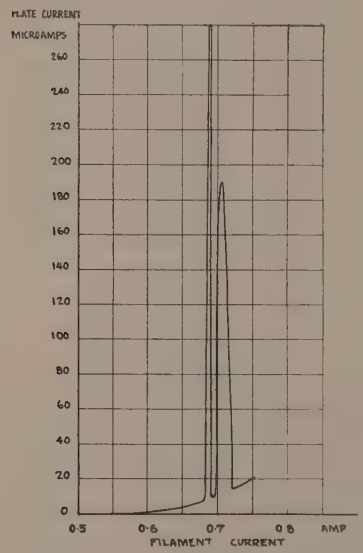

FIG. 10. *$I_p - I_f$ characteristic of Fotos R valve. $E_p = 0$ volts. $E_g = +180$ volts. $\lambda = 80$ and 89 cm. at lower and higher value of I_f, respectively.*

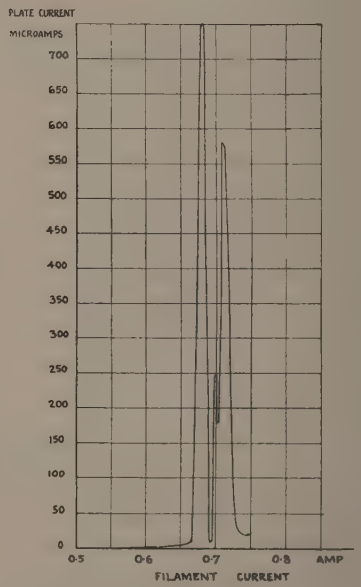

FIG. 11. *$I_p - I_f$ characteristic of Fotos R valve. $E_p = 0$ volts. $E_g = +202.5$ volts. $\lambda = 67$ cm. at peak of lowest I_f.*

The general form of the $I_p - I_f$ curves is somewhat of an exponential type, rising very steeply as the filament current is increased beyond the normal rated value. When the grid voltage is sufficiently high to produce oscillations, in the case of this valve about 25 volts or more, a very sharp and sudden increase of plate current occurs at certain values of filament current at which oscillations take place. This maximum occurs at higher values of filament current as the grid voltage is raised, the frequency of oscillation also increasing.

The decrease in wave-length as the grid voltage is increased, other factors remaining constant, is illustrated in Fig. 14. It is seen to be fairly uniform, practically linear in fact, with the exception of a few points. One cause of wide variation in results was the fact that the valve heated up very quickly at the higher grid voltages, so that readings taken while the valve was hot, or after it had been in operation some time, did not check with readings taken under similar circumstances while the valve was cold and had been standing idle for several days.

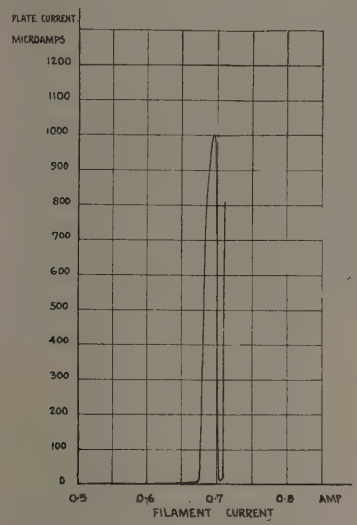

FIG. 12. *$I_p - I_f$ characteristic of Fotos R valve. $E_p = 0$ volts. $E_g = +225$ volts. $\lambda = 63$ cm. at peak.*

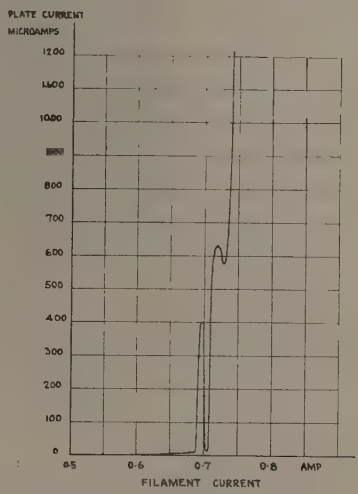

FIG. 13. *$I_p - I_f$ characteristic of Fotos R valve. $E_p = 0$ volts. $E_g = +225$ volts. $\lambda = 67$ cm. at both peaks.*

It will be noted that at the higher grid potentials there are two and in some cases three "resonance" peaks in the $I_p - I_f$ curve. It was found that oscillations at the several peaks were of different wave-lengths, shortest wave-length occurring at the peak of lowest filament current. The triple peaked curve of Fig. 9 could not be reproduced several days later under the same conditions, the smallest peak not appearing. The peaks move to the right as the grid voltage is increased, that is, higher filament current is required to produce oscillation at higher grid voltages. This is probably due to the fact that, as mentioned before, the normal or non-oscillating plate current becomes less as the grid voltage increases, so that the filament emission must be increased to produce oscillations.

At the highest grid voltages used the grid became white hot, thus supplying a secondary emission current to the plate. This plate current could be reduced by applying negative plate potentials, but this reduced the oscillations to zero if the negative plate voltage was sufficiently great. In Fig. 12 and 13 a further

I_p maximum was observed at higher filament currents, but as the grid became excessively hot and the rated normal filament current was considerably below these values, no readings were taken.

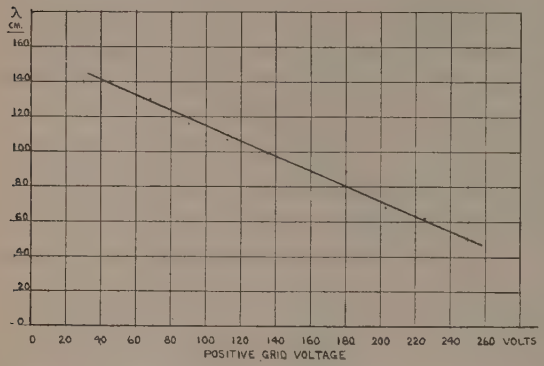

FIG. 14. *Variation of wave-length with grid potential. Oscillator using B-K circuit with Fotos R valve. $E_p=0$ volts.*

The whole I_p-I_f curve is more to the right when the filament is first lit, and the peak slowly shifts to the left after the valve has been in operation awhile. The effect produced is as though the filament current increased slightly as the valve warmed up. Thus this creepage may cause the plate current either to increase or decrease, depending upon the side of the peak to which the filament current is adjusted. The curves shown in the figures were taken under steady state conditions, that is, the valve was allowed to warm up before any readings were taken.

Further Experiments

The Fotos straight filament *R* valve was later placed in the circuit of Fig. 2 (*b*) and the condenser bridge across the grid and plate parallel wires omitted, leaving the circuit as in Fig. 3. It was found that oscillations could still be obtained with this circuit, the wave-length being about 60 to 70 cm. Oscillations were also obtained when the filament polarity was reversed, making the positive filament battery terminal the common connection. The curve of Fig. 13 was taken under these conditions, and it is evident that the removal of the condenser bridge did make some change in the circuit. However, the difference between the curves of Fig. 12 and 13, taken with and without the bridge, respectively, is not any greater than could be accounted for by the variation from day to day in results obtained from identical arrangements. The wave-length was the same for both peaks of the double-peaked curve of Fig. 13 whereas in the other multiple-peaked curves the wave-length decreased at the lower values of filament current. Oscillations were unstable, however, at the higher values of filament current in this case, as the valve became greatly overheated, and the wave-length measurement here was not very reliable.

The parallel grid and plate wires of the circuit of Fig. 3 were then removed, leaving only the Fotos *R* valve in its socket with the choke coils at each terminal. Oscillations were obtained as before, showing that the grid-plate condenser and its associated parallel wire circuit did not produce the oscillations. The wave-length remained the same as with the wires.

Discussion

The explanation given by Barkhausen for this type of oscillation does not explain the effects observed in the experiments outlined here. The usual explanation of a cloud of electrons oscillating back and forth between filament and plate, accelerated by the attraction of the grid, is insufficient to explain why the oscillations should occur at several definite values of filament current and not in between these values. Breit (2) describes the production of oscillations by a method somewhat similar to that used by the author but he obtains oscillations within only one narrow range of filament current, while in the author's experiments oscillations were found to take place over several very narrow ranges of filament current each about 15 to 20 m.a. wide. No satisfactory explanation was found by Breit, although several possibilities were suggested. The effect seems to resemble somewhat the numerous resonance potentials which are found in gaseous discharge tubes. The valves used in these experiments were all high vacuum tubes, however.

The change in wave-length as the filament current is increased and another point of oscillation is reached is insufficient to permit considering that oscillations now take place between grid and plate, or between filament and grid, instead of between filament and plate as at first. Also the wave-length increases with increasing filament current instead of decreasing, as would be the case if oscillations took place between grid and plate or filament and grid. This increase in wave-length or decrease in frequency as the filament current is increased, agrees with some theoretical calculations made by F. W. Sears (9). In an analytical investigation of Barkhausen oscillations Sears finds that the effect of increasing space charge is to decrease the frequency. Since the space charge is proportional to the filament current, this finding is in agreement with the experimental results of the author. The experimental results of most other investigators (1, 4, 8) disagree with this, however, and indicate the reverse to be the case, that is, frequency increases with increasing filament emission. It is possible that two distinct types of oscillation may occur, even under similar conditions, the effect of variation in space charge being opposite in the two cases.

If it is considered that the oscillations which occur at the lowest value of filament current take place in the interelectrode space between the plate and a layer at some distance from the filament, a possible explanation of the increase in wave-length with increasing filament current may be given. As the initial velocity of the electrons leaving the filament is increased by raising the filament current, they tend on rebounding from the plate to penetrate farther and farther into the cloud of electrons forming the space charge between filament and grid. Thus the path travelled in each cycle of oscillation increases in length, so that the time taken for each oscillation becomes greater and therefore the wave-length increases. This does not explain why oscillation takes place only at definite filament currents. Possibly the grid and plate elements act as tuned circuits, resonant at certain fixed frequencies whose values are determined by the capacity between the two, which is in turn dependent on the number of

electrons moving about in the interelectrode spaces. Thus if we consider the grid and plate each to have definite values of inductance, with which is associated the capacity between them, then this system will be resonant at some specific frequency. If the natural period of the system happens to correspond to the periodic time of a large number of the electrons travelling back and forth between filament and plate, stable oscillation of the electron cloud will be set up. If the filament current is now increased, the periodic time of both the electrons and the grid-plate circuit will be altered, so that they will no longer be in resonance and continuous oscillations will not be produced. As the filament current is further increased another point may be reached where they will again come into resonance and set up and maintain oscillations.

At the higher filament currents the electron cloud is denser, which means that the interelectrode capacity is greater and hence the wave-length correspondingly greater or the frequency less. This is what was actually found to be the case experimentally, the highest frequency occurring at the lowest filament current. The above explanation appears adequate, therefore, to fit the facts.

The author's results explain the action of an "electronic ampli-detector" described by K. Okabe (7). Okabe found that when using a receiver with a circuit of the Barkhausen type, the intensity of the received signal increased from zero to a sharp maximum and then decreased to zero again as the filament current of the receiver valve was varied from 0.62 to 0.63 ampere. The valve being in oscillation within this narrow region of filament current, as described herewith by the author, would explain the increased sensitivity of the receiver over the range of oscillation. The graph of received signal intensity versus filament current given by Okabe corresponds closely to the form of the author's $I_p - I_f$ curves.

Acknowledgment

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ON THE HYDROGENATION OF BITUMEN FROM THE BITUMINOUS SANDS OF ALBERTA II[1]

By E. H. Boomer[2] and A. W. Saddington[3]

Abstract

A second series of experiments on the batch hydrogenation of McMurray bitumen has been carried out. A cylindrical autoclave, of 1.8 litres capacity and designed for close temperature control and efficient agitation, is described.

Hydrogenation of the larger part of the bitumen proceeded with ease and commenced at comparatively low temperatures. The rate of hydrogenation was dependent on temperature, presence of a catalyst and extent of hydrogenation. The reaction commenced slowly at 200° C. and increased with rising temperature. The presence of molybdic anhydride approximately doubled the rate of reaction. The extent and rate of hydrogenation decreased on repeated runs with the same lot of bitumen due to the adverse effect of an increasing proportion of simple hydrocarbons.

An increase in the relative amount of hydrogen to bitumen increased the absolute rate of reaction and degree of hydrogenation possible in one treatment. As a result of the shorter time required, coke formation was largely suppressed.

Experiments on distillation residues from hydrogenated bitumen reveal the presence in bitumen of some 15% of asphaltic material which is very resistant to hydrogenation or cracking at temperatures as high as 500° C. This material has not yet been hydrogenated without considerable coke formation but the problem does not appear to be insoluble.

It appears that 75% of Alberta bitumen may be converted easily to gasoline and oil.

Introduction

The hydrogenation of carbonaceous materials such as coal, lignite, tar, etc., has been the subject of much investigation (4 (Chap. 44), 6) and a comparatively satisfactory technique has been developed in the past few years. As part of a project dealing with the utilization of the waste natural gases of Alberta, an investigation of the possibilities in a process of liquefaction by hydrogenation of Alberta bitumen was initiated. Natural gas affords an adequate and cheap source of the necessary hydrogen and the enormous extent (2) of the bituminous sands in Northern Alberta assure sufficient supply of the other raw material.

The first report of this series (1) presented preliminary results obtained with a high pressure autoclave of 850 cc. capacity. These early experiments showed conclusively that hydrogenation of bitumen was possible and resulted in a maximum oil yield of 80%, the remainder going to coke and gas. Owing to the design of the autoclave, uniform or even controlled temperature distribution was not possible and it was deemed advisable to investigate the process further in an autoclave of more appropriate design. It is the purpose of this report to present the results obtained with an autoclave more than twice as large and designed to allow of excellent agitation of its contents, as well as a maximum temperature variation of 10° C. over its length. In this manner, regions of

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high temperature and little agitation were eliminated and thermal decomposition to coke and gas minimized. The more precise experiments possible in this autoclave have confirmed and extended the original work.

Light crude oils have been produced and coke formation suppressed altogether at reaction temperatures up to 425° C. in hydrogenation of bitumen. The yield of gasoline is 20 to 30% and may be largely increased by successive hydrogenation of the oils remaining after the gasoline fraction has been removed. Lubricating oil and paraffin wax fractions can be obtained in considerable amount from bitumen by partial hydrogenation. As the results indicate the desirability of a continuous system of hydrogenation, an improved autoclave, more than twice as large, is being installed. It will be capable of continuous operation on liquid and gas phase hydrogenation, singly and combined.

The occurrence of two co-existent equilibria has been assumed in an attempt to account for the course of the reactions in the autoclave. One reaction is between bitumen and hydrogen, and the products of hydrogenation and the other is between bitumen and gaseous hydrocarbons, and the products of cracking. Increasing temperature favors the latter reaction more than the former. Careful temperature control is essential in the prevention of coke formation through the second reaction.

Materials

Bitumen, separated from the bituminous sands of the Fort McMurray area (2) and supplied by Dr. K. A. Clark of the Research Council of Alberta, was used as received. The properties of different lots of bitumen varied only slightly except in regard to water content. Before use, the bitumen was dehydrated by heating at 110-120° C. until evolution of steam ceased. The chief properties of the bitumen used are as follows:

Carbon	82.3%	Initial b.p.	175° C.
Hydrogen	10.2%	Carbon residue	14.2%
Nitrogen	0.37%	Density at 25° C.	0.998
Sulphur	4.2%		

Commercial electrolytic hydrogen was stored under pressure and used directly without treatment. In those experiments involving the use of natural gas, Viking field gas was used. This gas is dry, free from sulphur, and analysis shows it to be 93% methane. The balance is largely nitrogen with some ethane, propane, and 0.1% carbon dioxide.

Only two catalysts have been used in most of the present work; ammonium molybdate and molybdic anhydride prepared by ignition of the first-named substance. The ammonium molybdate had been found efficient in previous work and molybdic anhydride has been found equally efficient and introduces no ammonia. Anhydrous aluminium chloride was used as catalyst in one experiment.

Apparatus

The compression and gas storage system was essentially the same as before and consisted largely of standard equipment. Standard types (5) of joints and valves were used in which all seals were metal to metal. Pressures in the autoclave were measured by a Bourdon tube recording gauge calibrated at intervals by comparison with a standard test-gauge. Temperature measurements were made with calibrated iron-constantan thermocouples and a Leeds and Northrup recording potentiometer controller. This instrument gave a temperature control of $\pm 5°$ C.

The autoclave and its supporting apparatus that permitted agitation by oscillation of the furnace and autoclave is shown schematically in Fig. 1. The arrangement is similar to that described by Peters and Stanger (7). The autoclave shell, A, was machined from KA2 nickel-chromium steel and designed for service to 7500 lb. per sq. in. at 500°C. The shell was in the form of a tube and was closed at each end by a standard method (5) employing six bolts in compression, bearing on end plates, B, seated on a confined ring of soft copper. It was found advisable to protect the copper rings from the action of sulphur by aluminium rings of smaller diameter. Aluminium was not satisfactory alone at the high temperatures used. The stress was transmitted from the end plates to the shell through a ring nut, C, which was screwed into the shell by buttress threads. The ring nut and compression bolts were found satisfactory when made of chrome-vanadium steel. The end plates, B, were drilled and threaded in the centre of the outside faces, thus allowing of the use of a drawbar to assist in their removal. One end plate carried a thermocouple well, D, which extended co-axially inside the shell to its midpoint. A gas connection, E, was made to the shell at its midpoint as shown. The capacity of the autoclave when assembled was 1800 cc. It was readily opened by loosening the compression bolts about half a turn and screwing out the ring nut.

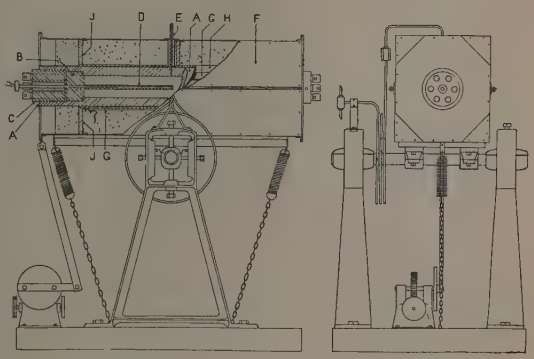

FIG. 1. *Diagram of high-pressure autoclave.*

The autoclave was supported in a split electric furnace, F, heated by five 500-watt strip heaters, G. These were spaced uniformly about the autoclave so that three were in the lower half of the furnace and two in the upper half. The furnace casing of sheet metal on a light angle iron frame carried the weight of insulation only. A split pipe, H, carrying the heaters, was bolted to steel cross members, J, which were supported by the base plate of the furnace. Both halves of the furnace were fitted in the same manner and the upper half

bolted to the lower half along an outside longitudinal flange. The autoclave fitted snugly within the two halves of the split pipe and rotation was prevented by two lugs which fitted into recesses in the pipe. The use of a metallic casing, in this case $\frac{1}{4}$ in. thick, through which the heat was transmitted to the autoclave, assisted in producing and maintaining a uniform temperature. The furnace was readily dismantled and the autoclave removed for examination when necessary. The installation of new strip heaters was accomplished by removal of the split pipe to which the heaters were bolted.

The base of the furnace was attached to two flat boxes fitted on a shaft which was supported at each end by inverted shaft hangers. An oscillating motion was imparted to the furnace and contained autoclave by a motor-driven reducing gear operating a crank and connecting-rod mechanism. The crank throw was 6 in. and 20 complete oscillations per minute were made. To ensure smooth operation of the mechanism, springs were stretched from each end of the furnace base to chains of adjustable length attached to the floor. The spring tension was adjusted to take most of the weight of the apparatus as it departed from the horizontal position.

Gas connection was made to the inlet, E, through a flexible copper coil of three turns, 12 in. in diameter, which was centered on the bearing shaft. The outer end of this coil was terminated by a T-connection, one branch leading to the pressure gauge, the other to a high pressure oil trap. From the oil trap the gas line was led to the gas compression system and a second line was led to the expansion valve, the outlet of which was connected to an oil filled wet-test gas meter and gas holder. Heat control of the autoclave was accomplished by adjusting the voltage on all or any of the strip heaters at 110-220 volts. A magnetic switch was operated by the potentiometer controller and produced the desired changes in voltage in accordance with the temperature variation.

Procedure

The experimental procedure was similar in most respects to that previously described (1). The quantities of bitumen were varied from 375 to 1200 gm. The charge of bitumen was added to the clean autoclave through one end and, after closure was effected, the apparatus was flushed with hydrogen. When a catalyst was employed, the powdered material was thoroughly incorporated into the bitumen before the charge was placed in the autoclave. No liners of any sort were used in the autoclave and no corrosion of the steel has occurred. Any catalytic effect of the steel was present in all experiments.

About two to three hours were required to heat the autoclave to the operating temperatures. Oscillation was commenced at 150° C. at which temperature the charge was fluid and reaction negligible. The temperature was maintained at a constant value until the pressure ceased to drop and on occasion, until the pressure had passed through a minimum and rising pressure gave evidence of cracking. The time to the minimum pressure varied from four to less than one hour as the temperature of experiment was changed from 380 to 450° C. After cooling overnight, the gas was released at the expansion

valve to the gas meter and thence to the gas holder from which samples were removed for analysis. Hydrogen sulphide was determined by allowing a definite volume of gas to bubble through standard iodine solution in a Meyer absorption tube inserted between the expansion valve and the gas meter. On occasion, condensers were inserted in the same place with the object of collecting the volatile hydrocarbons in the gas. Usually these hydrocarbons were removed by absorption in the oil of the gas meter. They amounted to 1.5 to 2% of the original bitumen and boiled below 40° C. This procedure was repeated from one to four times in different experiments before opening the autoclave. Each repetition, hereinafter, will be termed a cycle.

The product in the autoclave was removed and bottled as rapidly as was possible but losses always occurred due to evaporation of volatile hydrocarbons, which was assisted by some foaming. Moreover, a loss was occasioned by the film of oil remaining in the autoclave. Coke was determined by filtering the autoclave product and allowing the adhering oil to drain for some time. The coke yields are in general higher than actual because of incomplete removal of the oil by this process. The oil yield was consequently lower than the actual value on this account, in addition to those losses mentioned above. The hydrogen absorption was calculated from the difference between the quantity of hydrogen added to the cold autoclave and that recovered in the gas holder as given by the meter readings and gas analysis. The values are expressed in per cent by weight of the original bitumen.

The methods of oil analysis have been described in the previous report. In the present work, they were supplemented frequently by determinations of carbon and hydrogen and occasionally by nitrogen determinations. Nitrogen was determined by a modified Kjeldahl method (8) but sufficient data have not yet been obtained to indicate the fate of the nitrogen in the bitumen on hydrogenation. The few analyses that have been carried out show that the nitrogen content of the oils is about one-half that of the bitumen. Gasoline, kerosene, and gas oil were determined by distillation through an 18-in. fractionating column and occasionally the lubricating oil and paraffin wax fractions were obtained by vacuum distillation to 300° C. in the same column.

Results and Discussion

The details of individual experiments are presented in what follows as groups tabled together because of their value as comparative data. In some instances the course of individual experiments is illustrated by figures showing the changes of pressure with time and temperature.

The tables are in general self-explanatory, although some remarks may be appropriate in regard to certain values. Each addition of hydrogen, heating, cooling and removal of gas, is termed a cycle and each experiment on a sample of bitumen includes one or more such cycles. The row headed average time per cycle, refers to the time during which the autoclave was within 5° C. of the temperature of the experiment. This time does not give the total reaction time since hydrogenation commenced at some temperature below 350° C.

The gas analyses represent the mean of the analyses for each cycle, account being taken of the different volumes of gas in each cycle. Viscosity values are given in poises and were determined in an Ostwald pipette. The unsaturation value for the crude oil gives its solubility in 98% sulphuric acid and includes olefines, aromatics and unaltered bitumen. The data for crude and refined gasoline were found on the whole of the crude oil except the small part required for the other tests. Occasionally the gasoline yield was found from the A.S.T.M. distillation. Refining methods consisted in washing the crude gasoline in turn with 10% alkali, 80% sulphuric acid and 10% alkali and water. No attempt was made to remove sulphur which amounted to less than 0.5% in the gasoline. A stable, water-white gasoline was produced by the above process.

In regard to the yields of gas and coke, it is necessary to emphasize that the coke figures are high and the oil figures are low compared with the true yields. Oil remaining in the coke and evaporative losses both lower the yield found. A normal loss of 5 to 10% may be attributed to the oil fraction in experiments using 1200 to 700 gm. charges, and in those experiments using smaller charges, the mechanical losses are proportionately higher. Other sources of loss sometimes occurred due to leaks in the autoclave closures and excessive foaming of the product. Such experiments were all in the series using large charges and were obvious in that the loss tabled is greater than 10%. No leaks occurred in any of the tabulated experiments with the smaller charges.

Hydrogenation of Bitumen at 380 to 400° C.

The pertinent data of a number of experiments on 1200-gm. charges of bitumen at 380 to 400° C. are presented in Table I. Molybdic anhydride was added to the extent of 0.5% in all experiments but one.

Products of Hydrogenation

The yield of light oil, boiling below 350° C., varied from 40 to 60% as the temperature was raised from 380 to 400° C. This increase in oil production is evident from inspection of the A.S.T.M. distillation data. The crude and refined gasoline yields followed the temperature in the same manner. The other properties, such as density, viscosity, etc., paralleled the temperature and could be used as guides to the results of hydrogenation. By comparing Experiments No. 58 and 64, it will be seen that the catalyst had little effect on the properties of the oils. The sulphur content of the oils was less than half that of the bitumen, the difference appearing in the gas phase. The carbon dioxide occurring in the gas was somewhat high even when account was taken of the hydrogen sulphide which was included in the values. No explanation is forthcoming other than to attribute the carbon dioxide to the thermal decomposition of carboxylic acids in the bitumen. Water was not formed in visible amounts and this lends support to the idea that decomposition rather than hydrogenation of the acids takes place. The coke and gas production did not allow of any conclusions being drawn. It might be pointed out that the gas production was much larger in the absence of a catalyst.

TABLE I

HYDROGENATION OF BITUMEN IN 1200-GM. CHARGES AT 380° C. TO 400° C. IN THE PRESENCE OF MOLYBDIC ANHYDRIDE

	With MoO_3 as catalyst				Without catalyst
Experiment No.	58	59	60	61	64
MoO_3, %	0.5	0.5	0.5	0.5	0.0
Number of cycles	3	3	5	4	4
Time, hr. per cycle	3.0	3.3	3.6	2.5	2.5
Average temperature, ° C.	400	390	380	390	400
Average initial pressure, lb. per sq. in., cold	1637	1570	1448	1385	1105
Average maximum pressure, lb. per sq. in., hot	3437	2923	2910	2922	2363
Average final pressure, lb. per sq. in., cold	640	507	619	647	444
Pressure change per cycle, lb. per sq. in., cold	−997	−1063	−829	−738	−661
Hydrogen absorbed, % by weight of bitumen	1.1	1.1	1.3	1.1	1.0
Gas yield, less H_2, litres per kg. bitumen	33.2	40.2	36.4	40.4	57.2
Bitumen to oil, %	81.8	81.1	91.4	90.5	71.3
Bitumen to coke, %	5.2	7.2	0.0	0.0	7.2
Bitumen to gas, %	1.7	2.0	1.8	1.6	3.0
Loss, %	11.3	9.6	6.8	7.9	18.5
Bitumen to gasoline, %	26.1	16.6	13.8	17.0	23.0
Refined gasoline, %	18.1	13.5	11.6	13.1	19.6
Gas analysis, %					
CO_2	5.5	14.0	7.7	6.7	8.3
CnH_{2n}	1.6	2.6	1.7	1.9	1.7
H_2	34.3	31.3	56.4	51.4	24.3
C_2H_6	18.0	22.8	11.6	17.8	23.6
CH_4	28.6	18.1	10.1	14.3	31.0
H_2S	3.3	3.8	2.0	4.5	3.9
Oil properties					
Density, 25° C.	0.920	0.934	0.922	0.933	0.920
Viscosity, 25° C.	0.097	0.241	0.266	0.332	0.081
Carbon residue, %	8.1	10.0	7.2	9.0	12.5
Unsaturation, %	51	50	56	49	50
Sulphur, %	1.66	1.61	1.42	1.56	1.43
Initial b.p. ° C.	61	57	58	65	76
Per cent at 200° C.	24	17	17	17	24
Per cent at 300° C.	49	43	38	35	48
End-point, ° C.	326	313	310	318	361
C : H ratio	1.76	1.80	1.82	1.81	1.82
Pitch, %	40	50	59	59	36

Vacuum distillation, after gasoline removal, of the 400° C. oils yielded a kerosene and lubricating oil fraction amounting to 27% of the original bitumen. Refining of this distillate produced a straw yellow stable oil which was redistilled to yield 25% of its volume as lubricating oils. As an indication of the chemical nature of the oils produced, an analysis by the method of Egloff and Morrel (3) was carried out on the combined gasoline fractions. The method yielded the following results:

Unsaturated hydrocarbons	11.7%	Naphthenes	16.2%
Aromatic hydrocarbons	2.3%	Paraffins	69.8%

Presumably the crude oil as a whole would show larger relative percentages of the naphthenes and paraffins. Analysis of the crude oil showed it to contain about 15% bitumen.

It will be noticed in Table I that the hydrogen : carbon ratios are given as atoms of hydrogen per atom of carbon. These values were obtained with the A.S.T.M. distillate and vary only slightly from oil to oil. This slight variation is typical of all ultimate analyses on crude oils and various fractions. Appreciable variation did not appear among the different oils of corresponding fractions. Table II shows the result of an analysis carried out on the oils from Experiment No. 61 and may be taken as representative of all the oils.

TABLE II

ULTIMATE ANALYSIS OF OILS FROM EXPERIMENT NO. 61

	Crude oil	A. S. T. M.		Gasoline	Vacuum fraction to 250° C., less gasoline
		Distillate	Pitch		
Carbon	84.9	85.0	86.4	84.65	86.2
Hydrogen	11.85	12.7	8.7	14.2	11.65
Sulphur	2.38	1.42	—	0.5	—

Complete reduction of bitumen to gasoline involves the absorption of slightly more than 4% by weight of hydrogen. Less than half this figure appeared to be the maximum absorption in any one static experiment. It will be shown later that hydrogenation of the oil residues from distillation leads to a total absorption over 3% in some cases.

The crude oil showed an increase of 1.65% in hydrogen content and the hydrogen : carbon ratio was correspondingly higher. A discrepancy is apparent between the analysis of the crude oil and the weighted mean of the analyses on A.S.T.M. distillate and pitch and was due to loss of volatile hydrocarbons in the distillation. The small coke formation in Experiment No. 61, taken with the change in hydrogen content of the bitumen on hydrogenation to oil, shows without doubt that hydrogenation had occurred.

Pressure-time and Pressure-temperature Curves

In Fig. 2 and 3 are plotted the pressure-time and pressure-temperature curves of Experiments No. 58 and 64, respectively. They are quite similar to the corresponding curves of other experiments and are included merely as examples to emphasize general conclusions. These curves are of interest inasmuch as they give considerable information as to the course of the reaction in individual cycles and permit of some speculation as to the process of hydrogenation. The pressure-time curves give information as to the rate of hydrogen absorption and show clearly the point at which cracking predominates. The pressure-temperature curves represent a combination of the vapor-pressure curve of the bitumen and the effect of temperature on the pressure of hydrogen at constant volume. In the absence of hydrogenation reaction, the

slope of this curve should increase with temperature. Presumably, therefore, the point where this slope becomes constant or begins to decrease in value will indicate the initial stages of hydrogenation. This point, which is the beginning of the inflection of the pressure curve, defines the commencement of hydrogenation with some degree of precision. Other methods of plotting that are commonly used for vapor pressures are of little value. An inspection of curves B-1, Fig. 2 and 3, shows that hydrogenation of fresh bitumen began at 100 to 150° C. and rapid hydrogenation occurred above 300° C. In succeeding cycles, curves B-2, etc., the initial stages of hydrogenation commenced at slightly higher temperatures. The pressure measurements are not at present sufficiently precise to define this temperature with any great exactness. These curves end in a vertical line which represents the condition of constant temperature. In the first three cycles the pressure was dropping as the temperature was rising and at constant temperature the pressure continued to drop. In the fourth cycle, there was no drop in pressure, merely a small inflection in the curve followed by rising pressure at constant temperature. This indicates a considerable effect on the reaction with hydrogen of increasing quantities of light hydrocarbons in the oil.

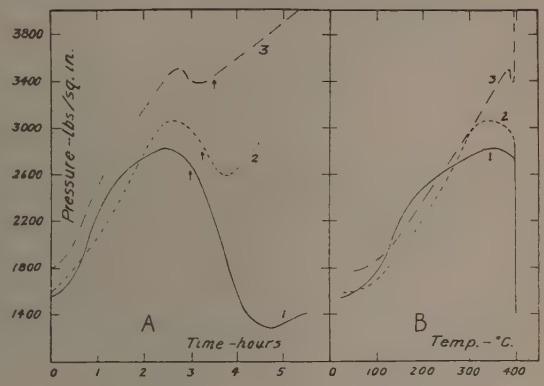

FIG. 2. *Experiment No. 58; A, pressure-time relations, B, pressure-temperature relations during hydrogenation at 400° C.*

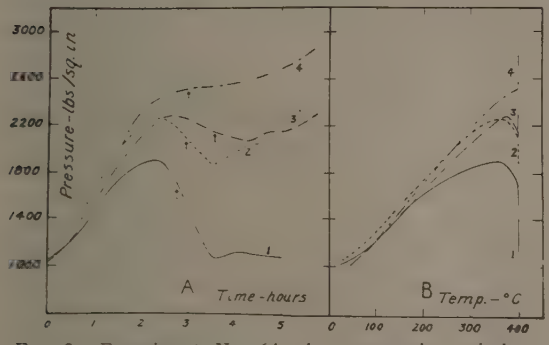

FIG. 3. *Experiment No. 64; A, pressure-time relations, B, pressure-temperature relations during hydrogenation at 400° C.*

Rate and Degree of Hydrogenation

The curves, A, of Fig. 2 and 3 show clearly the rate and to some extent the degree of hydrogenation. The time at which the temperature reached the constant reaction value is shown by an arrow on each curve. Evidently rapid hydrogenation commenced below 350° C. The rate of temperature rise was nearly constant but the pressure-time curve rapidly flattened out near 350° C.,

passed through a maximum and dipped to a minimum. There are some regular differences evident in these pressure-time curves in succeeding cycles. The magnitude of the pressure change and the rate of pressure change became less as the bitumen became hydrogenated. Moreover, the width of the minimum region decreased, and the rate of pressure increase subsequent to the minimum value increased with successive cycles. This was not unexpected in view of the greater probability of cracking as the bitumen becomes hydrogenated.

The greater part of the hydrogen absorption occurred during the hour previous to the attainment of reaction temperature and the hour immediately after. A marked retardation in the rate of pressure change occurred thereafter. These facts, in conjunction with the previous remarks on the pressure-temperature curves and the differences between successive cycles, suggest the presence of an equilibrium between the complex bitumen molecules and hydrogen on one side, and the smaller hydrocarbon molecules, resulting from the reaction, on the other. As hydrogen reacts with bitumen, its concentration falls and this decrease is accelerated by the addition to the gas phase of volatile hydrocarbons formed from the bitumen. Then, in a single cycle, it might be expected that the rate of reaction would decrease with time and in successive cycles, the maximum rate of reaction and its duration would decrease. An equilibrium as described is probable and somewhat similar ideas have received attention before (9, 10, 11) in dealing with cracking-still reactions. In the experiments under review, the equilibrium will be complicated by cracking reactions and a constant equilibrium pressure is not to be expected. Fresh bitumen behaves not infrequently in this manner, however, as inspection of curve A-1 of Fig. 3 will show. A study of the effect of hydrogen concentration and the removal of light hydrocarbons as formed should throw light on the matter and preliminary work on these lines is presented later.

Effect of Catalyst

A comparison of the slopes of curves A of Fig. 2 and 3 is of interest in bringing out the effect of a catalyst. Experiment No. 58 was carried out in the presence of molybdic anhydride and no catalyst was present in Experiment No. 64. The slopes of the decreasing pressure portion of curves A-1, Fig. 2 and 3, differ greatly. The slope in the first case is approximately 1100 lb. per hour as compared to 700 lb. per hour in the second case. The corresponding values for the second cycles of these experiments are 580 and 300 lb. per hour. Evidently the presence of a catalyst is beneficial in increasing the velocity of hydrogenation. The indications of a slow hydrogen absorption in the region 150 to 200° C. point to the desirability of further experiments with catalysts of greater activity than molybdic anhydride.

Hydrogenation at 400 to 445° C. on 700 to 1200-gm. Charges

Experiments at 400° C.

The data of representative experiments covering the temperature range, 400 to 445° C. are shown in Table III. Because of extensive cracking that

occurred at the higher temperatures, the charge of bitumen was reduced by stages to 700 gm. It was expected that the maximum pressure would be reduced and further that the available hydrogen would be maintained at a higher value. Coke production and cracking were decreased by this procedure and hydrogen absorption was increased. The suppression of cracking in the presence of sufficient hydrogen at 400° C. was brought out clearly by the absence of coke in Experiment No. 68. The gasoline yield was reduced, however, relative to the yield in Experiment No. 64 of Table I.

TABLE III

HYDROGENATION OF BITUMEN IN 700 TO 1200-GM. CHARGES AT 400 TO 450° C. WITHOUT ADDED CATALYST

	Cracking suppressed in presence of sufficient hydrogen	Low initial hydrogen pressure	Effect of increased hydrogen concentration counteracted by increased temperature		Time per cycle reduced by half; two additions of hydrogen	As in No. 84 but with smaller charge	Experiments at higher temperatures; cracking predominating	
Experiment No.	68	71	74	75	84	86	83	85
Bitumen, gm.	900	1200	915	910	885	710	910	710
Number of cycles	4	3	3	3	2	2	1	1
Time, hr. per cycle	3.5	2.5	2.5	3.0	1.5	1.5	1.0	2.0
Average temperature, °C.	400	400	425	425	425	425	445	440
Average initial pressure, lb. per sq. in.	1060	777	1153	1147	955	1000	1000	1000
Average maximum pressure, lb. per sq. in.	2238	2211	2676	2017	2190	2377	3960	2877
Average final pressure, lb. per sq. in.	499	439	555	580	671	645	640	610
Pressure change per cycle	−561	−338	−598	−567	−284	−355	−360	−390
Hydrogen absorbed, % by weight	1.5	0.5	1.4	1.3	0.6	1.0	0.5	0.8
Gas yield, less H_2, litres per kg. bitumen	54.3	44.6	106.5	89.7	55.4	77.3	66.5	87.2
Bitumen to oil, %	94.6	65.7	72.2	74.3	79.2	76.2	58.4	63.5
Bitumen to coke, %	0.0	16.7	10.4	8.2	7.9	12.0	21.8	18.4
Bitumen to gas, %	2.4	2.4	7.0	6.6	3.7	4.5	3.4	4.9
Loss, %	3.0	15.2	10.4	10.9	9.2	7.3	16.4	13.2
Bitumen to gasoline, %	17.4	17.1	32.5	37.9	25.0	29.9	29.2	31.8
Refined gasoline, %	13.9	13.6	28.3	28.2	20.6	25.1	23.4	25.6
Gas analysis, %								
CO_2	9.4	12.2	11.1	3.2	5.8	6.9	4.5	8.5
C_nH_{2n}	0.9	2.1	1.5	1.6	1.6	2.1	10.6	3.8
H_2	52.0	22.9	27.3	36.5	49.5	48.3	10.4	—
C_2H_6	16.7	29.4	39.6	15.8	23.6	—	27.0	36.8
CH_4	11.1	26.4	15.9	31.2	14.4	—	41.8	13.9
H_2S	11.0	5.8	2.3	2.0	4.6	3.8	4.3	6.1
Oil properties								
Density, 25° C.	0.927	0.941	0.903	0.904	0.929	0.918	0.903	0.898
Viscosity, 25° C.	0.319	0.134	0.034	0.038	0.102	0.054	0.024	0.028
Carbon residue, %	7.3	9.4	5.7	6.1	9.5	9.4	8.6	7.0
Unsaturation, %	—	40	35	34	60	44	43	42
Sulphur, %	1.68	1.95	1.25	1.16	1.85	1.58	1.68	1.84
Initial b.p. °C.	68	70	36	37	44	40	27	33
Per cent at 200°C.	16	24	39	39	27	32	43	43
Per cent at 300°C.	38	48	65	63	51	58	65	67
End-point, °C.	363	337	338	320	336	314	340	342
Pitch, %	34	18	24	26	22	27	24	19

Effect of Low Initial Hydrogen Pressure

Experiment No. 71 was designed to illustrate the effect of a low initial hydrogen pressure and is only of partial value because of a leak that occurred in one cycle. This caused a loss of volatile material and an increased coke production. There is, however, a decided drop in gasoline production as compared with Experiment No. 64 which is, in part, real. The loss in gasoline due to the leak would be balanced to some extent by that produced in cracking to coke.

Experiments at 425° C.

Effect of Increased Hydrogen Concentration

Three experiments, No. 74, 75 and 84, on 900-gm. charges and one, No. 86, on a 700-gm. charge, are reported for 425° C. The first two experiments are almost identical in most respects except with regard to the gas analysis. Inexplicable variations in the gas analyses from different experiments frequently occurred. The analyses of successive cycles in one experiment varied, however, in a regular and expected manner. In Experiment No. 84, the time per cycle was reduced by half and only two additions of hydrogen were made. There is evident a small decrease in coke yield and a large decrease in the hydrogen absorption. It may be concluded from this experiment that increasing hydrogen concentration does not cause an acceleration of the reaction equivalent to that produced by a catalyst. The results of Experiment No. 86 do not show any great differences from those of the preceding experiments. Gasoline production was higher and the hydrogen absorption was greater although the time per cycle was unchanged. The oil produced was of distinctly better quality. The shorter time per cycle is almost counteracted by the use of a smaller charge.

In general, coke production at 425° C. amounted to 10% and refined gasoline production was 25 to 30% of the bitumen as compared to zero and 15 to 20% for the same data at 400° C.

Experiments at 440 and 445° C.

Two experiments, No. 83 and 85 at 445 and 440° C. respectively, are reported. The losses were high and detracted from the value of the experiment. The gasoline production was much the same as at 425° C. and the hydrogen absorption was less. The large gas and coke production show that cracking predominated and was responsible for most of the gasoline. There was a distinct improvement in the oil quality as shown by all properties except unsaturation. The gas analyses in these experiments are inexplicable in showing 10% or less of hydrogen and bearing little resemblance to one another.

Properties of Oils Produced by Hydrogenation

The properties of the oils produced in this series of experiments reveal some interesting results. Generally, the density, viscosity and initial boiling point decreased with rising temperature. The coke and gasoline yields increased rapidly between 400 and 425° C. but the increase was only slight between

425 and 445° C. The yield of oils boiling above 225° C. was greatly decreased as the temperature rose but their quality was greatly improved in regard to bitumen content. Kerosene and gas oil made up 25 to 30% of the crude oils produced at 425° C. and the remainder contained 10 to 12% of the crude oil as lubricating oils and paraffin wax. This lubricating oil fraction was obtained by vacuum distillation to 325° C. Higher temperatures were not employed as decomposition commenced and a solid, high melting-point wax interfered in the condenser. The pitch remaining in the still was asphaltic in nature, being insoluble in hot petroleum naphtha and 99.5% soluble in carbon disulphide. The lubricating oil fraction was of a fluorescent green color and almost transparent. The oil did not change appreciably on standing except for a slight reddening in color. A separation of the paraffin wax content was impossible due to its poor crystal form. Chilling precipitated the wax as a green mud, estimated at 50% by volume of the total fraction, and left a clear green supernatant oil having no fluorescence.

Effect of Temperature on Rate of Hydrogenation

An inspection of Fig. 4 showing the pressure-time curves of Experiments No. 68 and 74, makes it evident that hydrogenation occurred more rapidly at 425 than at 400° C. Only the first cycle of these comparable experiments is shown and the arrows indicate the time when constant temperatures of 400 and 425° C. were reached. There was no leak in either of these cycles. The rate of hydrogenation, as given by the slope of the curve after constant temperature had been reached, increased continuously to at least 425° C. The ultimate course of the pressure-time curves differed markedly. In less than one hour at 425° C. the pressure rose steadily as cracking occurred and at 400° C. the pressure dropped slowly to a constant value. A definitely increasing pressure has not been found to occur with fresh bitumen at 400° C. in the absence of leaks. With partially hydrogenated bitumen such as is present in second and succeeding cycles, cracking occurred and the pressure rose indefinitely.

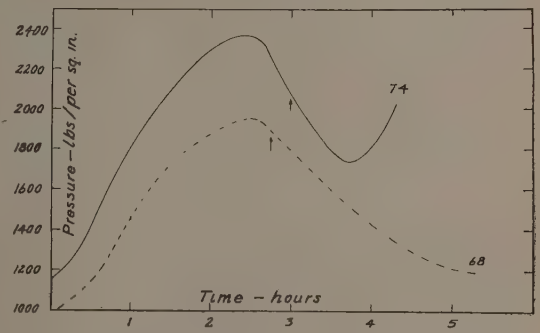

FIG. 4. *Pressure-time relations in initial cycles of experiments No. 68 at 400° C. and No. 74 at 425° C.*

The pressure-time curves of Experiments No. 83 and 85 are not presented. They resemble the curve for Experiment No. 74, Fig. 4, with the difference that the depression in the curves is much smaller. The pressure was rising again at 430° C.

Effect of Concentration of Hydrogen

It would appear that the concentration of hydrogen is an important factor among the conditions governing hydrogenation and cracking. A large reduction in the hydrogen concentration, such as occurs through hydrogenation, allows cracking to begin. The higher the temperature, the smaller becomes the allowable reduction in hydrogen concentration that will retard cracking. The logical conclusion follows that a continuous process is advisable in which the hydrogen concentration can be maintained at a high value.

Pressure-temperature Curves

The pressure-temperature curves of this series need not be considered. They are typified by the corresponding curves of Fig. 2 and 3. At 425° C. and higher, the curves resemble those of the third and fourth cycles at 400° C. The curves pass through a shallow minimum, and at constant reaction temperature rise indefinitely.

HYDROGENATION WITH 400-GM CHARGES OF BITUMEN AT 400 TO 450° C.

Further Data on the Effect of Concentration of Hydrogen

To investigate further the effect of the amount of available hydrogen, a number of experiments were carried out using approximately 400-gm. charges of bitumen at temperatures of 400, 425 and 450° C. There was available a volume of hydrogen equal to 1200 cc., more or less, which at the common initial pressure weighed about 10 gm. or 2.5% of the bitumen. Two of the five experiments reported were run with a catalyst; in one case, 5% of molybdic anhydride, in the other, 4.4% of ammonium molybdate. Only one cycle was carried out in each experiment and the time of reaction was four hours at 400 and 425° C. At 450° C. the time was shortened to two or three hours because of excessive cracking. Table IV presents the details of these experiments and shows beyond doubt the beneficial effect of increased available hydrogen.

Coke production was very much decreased and the light oil fraction, boiling below 300° C., was as much as 40% of the original bitumen on one addition of hydrogen. The hydrogen absorption in one cycle was as great as that obtained previously in several cycles. In these experiments, no leaks occurred and the recorded losses must be assigned to poor recovery of liquid and, to a small extent, gaseous products. The loss of solid products may be considered negligible and the error in the determination of gaseous carbon cannot be more than 2.0%. Substances such as butane and pentane were probably formed in large amounts. Some could be recovered from the gas but no doubt the greater part was lost during removal of the oil from the autoclave. The conversion of bitumen to gaseous hydrocarbons was very large in all these experiments. At 400 and 425° C. it was of the same order as that produced in the series on larger charges after several cycles and at 450° C. it was much greater. It would appear that the conversion to gaseous hydrocarbons is controlled by the concentrations in the gas phase as well as by temperature and time. A relation between the degree of hydrogenation and the production

of gaseous hydrocarbons is to be expected if an equilibrium exists. Consequently, the gas production would not depend on the number of cycles but on the equilibrium concentration of the various reactants and the volume of the gas phase.

Influence of Molybdic Oxide and Ammonium Molybdate

The addition of molybdic anhydride at 425° C. accelerated the reaction and permitted the complete suppression of coke formation. An increased hydrogen absorption and gasoline production was also apparent in Experiment No. 109.

TABLE IV

HYDROGENATION OF BITUMEN IN SMALL CHARGES AT 400 TO 450° C.

	Effect of amount of available hydrogen					
	No catalyst	No catalyst	With catalyst, MoO_3	No catalyst	No catalyst	With catalyst, $(NH_4)_2MoO_4$
Experiment No.	106	105	109	104	107	108
Bitumen, gm.	475	462	400	461	375	455
MoO_3, %	0	0	5.0	0	0	0
$(NH_4)_2MoO_4$, %	0	0	0	0	0	4.4
Number of cycles	1	1	1	1	1	1
Time, hr. per cycle	4	4	4	2	3	2
Average temperature, ° C.	400	425	425	450	450	450
Average initial pressure, lb. per sq. in.	1325	1280	1145	1280	1280	1190
Average maximum pressure, lb. per sq. in.	2570	2148	1963	2524	2380	2290
Average final pressure, lb. per sq. in.	910	645	487	722	755	694
Pressure change, lb. per sq. in.	−415	−635	−658	−558	−525	−496
Hydrogen absorbed, % by weight	0.7	1.1	1.5	1.4	1.3	1.2
Gas yield, less H_2, litres per kg. bitumen	47.4	81.3	91.0	159.0	192.0	131.0
Bitumen to oil, %	92.7	79.2	85.0	51.0	54.7	57.2
Bitumen to coke, %	0.0	7.6	0.0	11.9	6.7	15.4
Bitumen to gas, %	2.9	5.3	5.1	10.0	12.8	9.1
Loss, %	4.4	7.9	9.9	27.1	25.8	18.3
Bitumen to gasoline (A.S.T.M.), %	11.1	25.4	29.0	—	28.4	29.2
Gas analysis, %						
CO_2	3.1	3.8	7.4	3.6	5.3	4.9
C_nH_{2n}	1.5	2.3	2.3	2.2	3.4	2.3
H_2	75.5	46.7	35.9	29.4	36.5	30.4
C_2H_6	4.5	25.8	28.0	37.4	34.2	45.3
CH_4	9.1	9.5	14.9	19.2	15.5	11.9
H_2S	3.6	6.0	6.6	—	1.3	—
Oil Properties						
Density, 25° C.	0.955	0.925	0.911	—	0.916	0.908
Viscosity, 25° C.	—	0.088	0.069	—	0.028	0.030
Carbon residue, %	10.5	8.0	11.9	—	10.5	8.4
Unsaturation, %	78	48	42	—	42	35
Sulphur, %	2.53	1.95	1.76	—	2.11	2.25
Initial b.p., ° C.	72	57	60	—	47	46
Per cent at 200° C.	9	24	27	—	45	44
Per cent at 300° C.	27	52	54	—	65	67
End-point, ° C.	340	345	332	—	355	363
Pitch, %	47	30	32	—	25	21

The quality of the crude oil showed a slight improvement when compared to that produced in Experiment No. 105. The use of ammonium molybdate at

450° C. does not appear to be entirely beneficial in view of the increased coke production in Experiment No. 108 compared to No. 107. The gas yield and the production of volatile hydrocarbons in the presence of this catalyst show a decided decrease and the oil is of better quality. On the whole, no decision can be made at present as to the value of a catalyst at these temperatures.

Rate of Hydrogen Absorption

The pressure-time curves of Experiments No. 104, 105 and 106 are shown in Fig. 5. It is evident that the rate of hydrogen absorption increased with rising temperature and only at 450° C. did cracking occur leading to an ultimate pressure rise. This is contrary to experience at 425° C. with larger charges of bitumen (Fig. 4). To illustrate clearly the effect of available hydrogen, Fig. 6 is shown on which are the pressure-time curves for the first cycles of Experiments No. 74, 86 and 109. These experiments were all performed at 425° C. but the charge differed in each case, 915, 710 and 400 gm. respectively, being used. The maximum pressure developed, taking into account the differing initial pressures, dropped by approximately 70 lb. per sq. in. per 100 gm. decrease in weight of charge. The rate of hydrogen absorption as given by the average slope of the curves in the decreasing pressure region was 520 lb. per hr. for Experiment No. 74, 235 lb. per hr. for Experiment No. 86, and 360 lb. per hr. for Experiment No. 109. The absolute rates of hydrogen absorption in grams of hydrogen per gram of bitumen per hour, were in the ratio, 0.4 : 0.3 : 1.0 for the experiments in the order named. Evidently, there is a distinct saving in time to be gained in the use of relatively large amounts of hydrogen whereby the hydrogen concentration is maintained at a high figure.

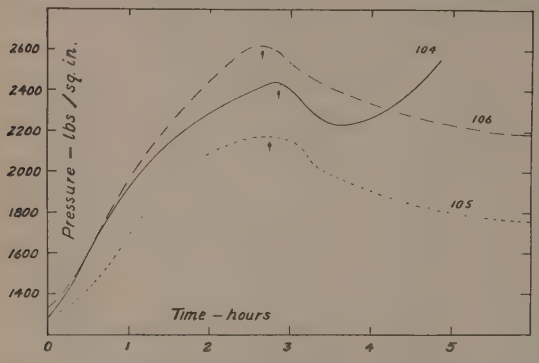

FIG. 5. *Pressure-time relations in Experiments No. 104 at 450° C., No. 105 at 425° C. and No. 106 at 400° C.*

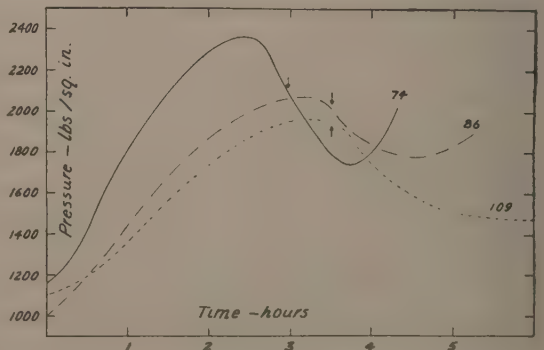

FIG. 6. *Pressure-time relations during hydrogenation of varying weights of bitumen. No. 74—915 gm.; No. 86—710 gm.; No. 109—400 gm.*

Hydrogenations at Different Initial Partial Pressures of Hydrogen

A number of experiments were performed at 425° C. on 900-gm. charges of bitumen in which the hydrogen was diluted with Viking natural gas. These experiments had for their object the determination of the minimum hydrogen concentration at which hydrogenation would proceed satisfactorily. Two other experiments, No. 89 and 90, are included for comparative purposes. Experiment No. 89 was a straight cracking run in which the pressure developed was the thermal pressure only. Experiment No. 90 was of the same nature with the difference that an initial pressure of 400 lb. per sq. in. of Viking gas was used. The other three experiments were started with three different mixtures of hydrogen and natural gas as tabulated. The total initial pressure was 1000 lb. per sq. in. and one cycle was run in each case. The experimental data are shown in Table V.

TABLE V

Hydrogenation of bitumen at various hydrogen concentrations in one cycle

	Straight cracking	Experiments with varying amounts of natural gas			
Experiment No.	89	90	92	91	93
Bitumen, gm.	925	925	920	900	900
Temperature, °C.	420	425	425	425	425
Natural gas, lb. per sq. in.	15	400	333	500	667
Hydrogen, lb. per sq. in.	0	0	667	500	333
Total initial pressure, lb. per sq. in.	15	400	1000	1000	1000
Maximum pressure, lb. per sq. in.	2560	2920	3120	3900	3700
Final pressure, lb. per sq. in.	650	810	800	840	1080
Pressure change, lb. per sq. in.	+635	+410	−200	−160	+80
Time, hr.	2	1	1.5	1.5	1
Hydrogen absorbed, % by weight	—	—	0.4	0.2	0.2
Gas yield, less added gases, litres per kg. bitumen	49.3	—	57.1	—	59.5
Bitumen to oil, %	63.8	68.1	73.9	68.4	74.0
Bitumen to coke, %	18.9	18.9	16.3	18.9	15.5
Bitumen to gas, %	3.2	—	3.3	—	3.2
Loss, %	14.1	8.4	5.4	7.3	5.1
Bitumen to gasoline, %	26.0	25.0	26.9	27.9	28.7
Refined gasoline, %	20.1	21.5	22.6	23.0	24.0
Gas analysis, %					
CO_2	7.3	8.6	9.7	8.2	6.4
C_nH_{2n}	3.0	2.9	2.3	2.9	2.1
H_2	3.0	0.0	6.0	3.1	6.3
C_2H_6	45.5	42.7	41.7	33.4	34.4
CH_4	32.0	32.5	31.0	42.4	42.7
H_2S	5.7	5.1	4.4	3.3	3.4
Oil Properties					
Density, 25° C.	0.926	0.936	0.931	0.919	0.933
Viscosity, 25° C.	0.056	0.093	0.072	0.048	0.101
Carbon residue, %	11.4	12.0	9.6	10.2	11.4
Unsaturation, %	38	62	57	66	57
Sulphur, %	2.90	3.03	2.87	2.87	2.98
Initial b.p., °C.	40	43	37	36	42
Per cent at 200° C.	34	29	29	36	27
Per cent at 300° C.	59	54	54	59	51
End-point, °C.	335	318	340	338	336
Pitch, %	22	37	29	24	31

These experiments were of a preliminary nature only and served merely as indications of what might be expected. Other experiments under different conditions remain to be carried out. At present, more information can be obtained from the results of the work reported in previous sections on the effect of hydrogen concentration.

Experiments No. 89 and 90 were very similar in many respects. The effect of the natural gas added in the second experiment appeared in a reduction of the conversion of bitumen to gas and volatile hydrocarbons. The crude oil was heavier, more viscous and less volatile. The remarkable similarity of the gas produced in these experiments is hardly to be expected. The effect is not new and has been found in other unpublished work using various pressures of natural gas. That the final relative partial pressure of methane should be independent of the initial pressure, suggests a reversible equilibrium between the gaseous and liquid products of the cracking process such as proposed by Wilson (9, 10, 11).

The high boiling point of the bitumen was very clearly shown in all the experiments such as No. 89. The pressure became appreciable, about 25 lb. per sq. in., at 370° C. The pressure rose only slightly faster than the temperature until 400° C. was reached when decomposition apparently set in. The pressure rose thereafter at the rate of 700 lb. per hr. at any temperature between 400 and 425° C. The sulphur content of the gas was remarkably high and exceeded the quantities common in hydrogenation experiments. Apparently the conversion of the sulphur in the bitumen to hydrogen sulphide is not due to hydrogenation but is the result of pyrolytic decomposition, and hydrogenation may have an adverse effect by increasing the stability of the sulphur compounds.

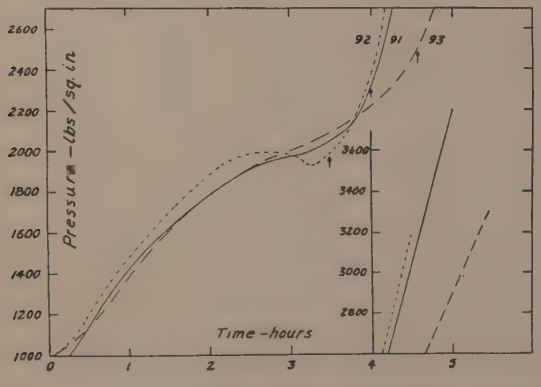

FIG. 7. *Pressure-time relations during hydrogenation with varying initial concentrations of hydrogen. No. 92—67% ; No. 91—50% ; No. 93—33% .*

Referring to experiments No. 91, 92 and 93, it is at once evident that reduction of the hydrogen concentration had a serious effect on the reaction. The oil yields were down and the coke yields were up compared to the experiments of Table III. The pressure-time curves shown in Fig. 7 illustrate graphically the decrease in hydrogen absorption. Only in Experiment No. 92, using 66.7% hydrogen, was a pressure drop evident. Under the conditions of these experiments, an initial hydrogen concentration greater than 50% was necessary for appreciable hydrogenation. The lower limit was undoubtedly less than 50%

in the light of the residual gas analyses; but this lower limit was rapidly reached when the initial hydrogen concentration was about 50%.

The results of the oil and gas analyses did not show any marked differences between these experiments. Experiment No. 93 did show greater resemblance to Experiments No. 89 and 90 than to the other two. Moreover, the maximum and final pressures, hydrogen absorption, coke production, gas yield and gas analysis, definitely separated Experiment No. 92 from No. 91 and 93.

Hydrogenation of Residual Oil and Pitch

The success of a continuous process for hydrogenation of bitumen will depend on two factors. One, the hydrogen concentration, has been discussed. The second involves the reduction of all the bitumen to oils without coke formation in serious amount. Preliminary to the establishment of apparatus in which hydrogen and bitumen may be added and the products of the reaction withdrawn in a continuous manner, experiments were carried out on oils and pitches remaining after distillation of the crude oils produced in the experiments reported. These residual oils and pitches contained all of the asphaltenes, tar acids and bases, and high boiling hydrocarbons not removed by the distillation process. They also contained those portions of the original bitumen most resistant to hydrogenation. Hydrogenation of these residues should indicate the possibilities of a continuous process by giving information as to the total conversion to oil probable.

The experimental details are given in Table VI. A variety of residues were employed and their origin is given by the first figure of the experiment number. This figure refers to the tables of previous sections in which are given the history and properties of the crude oils serving as sources of the residues under consideration. The crudes listed in these tables, together with those of the same series not listed, were distilled to various temperatures at different pressures and the residues combined to make up the charges of the experiments in Table VI. The temperature and the pressure at which distillation ceased is tabulated for each experiment under "Initial b.p. of charge." The amount of residue is referred back in each case to the bitumen from which it was derived. This figure is approximate only and is tabulated as "Per cent of original bitumen." An approximate calculation has been shown in the last line of Table VI which gives the fraction of the original bitumen remaining as pitch or pitch and coke. This figure represents the ultimate residue that is difficult to hydrogenate. It does not include any coke produced in the primary hydrogenation. Coke formation with bitumen may be suppressed entirely at 425° C., and minimized at 450° C. It is believed that the coke production is largely accidental and originates in substances that are easily decomposed and hydrogenated. The pitches produced were very stable and did not decompose at temperatures above 400° C. at atmospheric pressure, whereas cracking always occurred with the oils at 300 to 350° C.

The charges varied from a fluid oil in Experiments No. 3-1, 3-2, 4-1 and No. 1-1A, to a brittle pitch melting above 200° C. in Experiment No. 3-3.

TABLE VI

HYDROGENATION OF RESIDUAL OILS AND PITCH

Nature of charge	Crude oils less gasoline only		Heavy oil residue; catalyst, MoO_3	Soft pitch m.p. 30-40°C.	Crude oil from 1-1	Hard pitch m.p. near 70° C. catalyst, MoO_3	Brittle pitch, m.p. above 200°C.	Pitches softening at 30-40°C. catalyst, MoO_3	Hard pitch, m.p. near 70° C., catalyst, $AlCl_3$
Experiment No.	3-1	3-2	4-1	1-1	1-1A	1-2	3-3	3-3A	1-3
Charge, gm.	925	725	350	1200	900	408	385	257	347
Catalyst, %	—	—	5	—	—	5	5	5	7
compound			MoO_3			MoO_3	MoO_3	MoO_3	$AlCl_3$
Initial b.p. ° C.	225	225	300	250	65	250	325	—	250
of charge, mm. Hg	700	700	700	25	700	25	25	—	25
Per cent of original bitumen	50	34	36	38	38	36	15	15	22
Number of cycles	2	1	1	4	3	1	1	1	1
Time, hr. per cycle	3	3	3	3.5	3.3	1.5	3	1	2
Average temperature, °C.	420	450	450	400	425	470	450	500	460
Average initial pressure, lb. per sq. in.	1000	1000	1055	1150	1200	1020	1020	1055	1100
Average maximum pressure, lb. per sq. in.	2185	2890	2055	2120	2590	1960	1825	1970	1960
Average final pressure, lb. per sq. in.	770	800	595	445	550	750	490	625	495
Pressure change per cycle	−230	−200	−460	−705	−650	−270	−530	−430	−605
Hydrogen absorbed, % by weight	0.5	0.5	1.3	1.0	1.3	1.3	1.5	2.2	1.9
Gas yield, less H_2, litres per kg. charge	37.6	85.0	84.0	37.1	67.0	139.0	104.0	180.0	118.0
Oil yield, %	86.3	73.9	86.7	92.0	74.5	40	71.4	69.3	53.0
Coke yield, %	0.0	0.0	2.2	2.8	12.8	31	0.0	small	25.7
Gas yield, %	2.0	4.8	3.5	1.7	3.3	7.9	4.5	7.8	7.4
Loss, %	11.7	21.3	7.6	3.5	0.0	21.1	24.1	20.9	13.9
Gasoline yield, %	15.8	16.7	21.0	15.5	22.6	10.0	—	—	13.8
Gas analysis, %									
CO_2	1.6	2.6	0.4	7.0	4.2	1.1	1.2	0 9	0.1
C_nH_{2n}	1.4	2.4	0.8	1.1	1.2	0.3	0.9	1 7	0.3
H_2	61.9	20.8	55.3	20.4	43.2	29.8	31.2	34 8	35 0
C_2H_6	16.0	29.1	15.4	22.0	22.0	29.2	19.4	28 2	33 6
CH_4	11.7	40.4	14.8	32.6	13.8	29.1	28.0	21.6	22.4
H_2S	1.5	2.4	—	2.3	1.0	—	—	—	—
Oil properties									
Density, 25° C.	1.00	1.06	0.988	1.04	0.952	—	—	—	—
Viscosity, 25° C.	0.515	—	0.003	—	0.129	—	—	—	—
Carbon residue, %	16.1	25.4	13.0	20.6	8.4	—	—	—	—
Unsaturation, %	58	86	74	—	55	—	—	—	—
Sulphur, %	1.7	2.2	—	1.65	0.77	—	—	—	—
Initial b.p., °C.	65	60	60	58	52	65	—	105	55
Per cent at 200° C.	12	17	19	13	25	14	—	—	19
Per cent at 300° C.	37	39	41	28	46	—	—	—	45
End-point, °C.	343	357	330	335	343	255	—	—	390
Per cent pitch	36	41	39	41	37	65	—	—	30
Pitch plus coke as per cent bitumen	16	10	14	16	16	20	—	—	9

Pitches that softened between 30 and 40° C. were used in No. 1-1 and 3-3A and a hard pitch used in No. 1-2 and 1-3 melted near 70° C. The asphalt content, as given by the A.S.T.M. method, ranged from 25% in the oils to

over 99% in the brittle pitch. The amount of catalyst in the charge as tabulated does not take into account any catalyst remaining from primary hydrogenations.

Crude Oils Less Gasoline Only

Experiments No. 3-1 and 3-2, on crude oils less gasoline only, require little comment. They show a gasoline production slightly less than that in the primary hydrogenation. The loss was rather large in each case and represented a further yield of light oils. Although the oil produced was not as good, the pitch content was much smaller than in the primary hydrogenation. The higher temperature and smaller charge in Experiment No. 3-2 reduced the pitch content to the greatest extent. It is interesting to note the absence of coke formation in both these experiments.

Heavier Oil Residue with Molybdic Oxide

Experiment No. 4-1 on a slightly heavier oil residue resembled the above experiments. The hydrogen absorption was, however, nearly three times as great which indicated an adverse effect on hydrogenation by the light oils in the charges of Experiments No. 3-1 and 3-2. On the other hand, the presence of molybdic anhydride and the small charge may account for the increased hydrogen absorption. The gasoline production was higher and the maximum pressure lower as would be expected in either case.

Successive Hydrogenations of Soft Pitch from Light Crudes

Experiments No. 1-1 and 1-1A were successive hydrogenations of the same charge. The first experiment was with a soft pitch residue from vacuum distillation to 250° C. of the lighter crudes of Table I. The second experiment was on the crude oil resulting from the first experiment, less the amount required for the ordinary tests. The most notable feature was the constancy of the pitch and coke residue referred to the original bitumen. The pitch content of the charge was decreased only slightly in the second experiment while the gas and coke yield increased greatly. The further production of gasoline was small. The oil obtained in the second experiment was much improved as compared to the charge. The charge, the product of Experiment No. 1-1, was so viscous that viscosity and unsaturation determinations were not possible. It would appear that hydrogenation in the second experiment was almost wholly confined to the oil and did not affect materially the asphaltic substances.

Hydrogenation of Hard Pitch from Heavier Crudes.

Experiment 1-2 was carried out with a small charge of hard pitch from the heavier crudes of Table I. A higher temperature and a catalyst were employed in an endeavor to reduce the pitch residue. Hydrogen absorption was rapid and large, but coke and gas production were very great. The product was a mixture of viscous pitch and lump coke. A small quantity of water was formed and the odor of ammonia was very noticeable. The proportions of oil and coke were approximate and the large loss was unavoidable because of the difficulty in removing the product from the autoclave. The liquid portion was very unstable and commenced to crack at 240° C. on distillation. Cracking

ceased at 255° C. with 35% distilled over. The remainder was a brittle pitch of very high boiling point. This experiment showed strikingly the resistance of part of the asphaltic material in bitumen to hydrogenation. Apparently destructive cracking of the asphalt occurs before hydrogenation begins. It is noteworthy that water has not been found in the products of any previous experiment and ammonia has only been found in traces, and indicates the deep-seated change in the nature of the reactions in this experiment.

Hydrogenation of a Brittle Pitch

Experiment No. 3-3 on a very brittle pitch illustrates the great stability of these residual asphaltic materials. No hydrocarbons soluble in gasoline were present in this charge. No oil or coke production occurred on hydrogenation with molybdic anhydride at 450° C. The hydrogen absorption was real and the high loss was due to material left in the autoclave. The recovered material was very viscous and sticky. Its softening point was about 30° C. and its initial boiling point was above 200° C. The product of Experiment No. 3-3 was subjected to hydrogenation again in Experiment 3-3A at 500° C. A large hydrogen absorption occurred and the product was distinctly more fluid than the charge. A small amount of finely divided coke was suspended in the liquid. Considerable water, 5 to 7 cc., and ammonia were formed. The liquid was still viscous and extraordinarily sticky and tenacious. Distillation was impossible on account of excessive foaming of the liquid into the condenser and receiver. Repeated trials did not reduce the foaming to any extent. The initial boiling point of 105° C. tabulated is probably too high.

Hydrogenation of Hard Pitch with Aluminum Chloride as Catalyst

The last experiment, No. 1-3, on a hard pitch as used in No. 1-2, was carried out with aluminium chloride as catalyst. This catalyst is more destructive in its action than molybdic anhydride and the results confirm this in showing a degree of success as compared to Experiment No. 1-2. The coke product was not very different in amount but appeared in a finely divided form. Water was formed in small amounts and was acidic. Considerable quantities of hydrogen chloride were present in the gas and oil. The oil was quite fluid and yielded gasoline amounting to 14% of the charge. Its behavior on distillation was very interesting. A small amount of cracking occurred at 300° C. and then ceased. Boiling continued quietly thereafter even when the still was above 450° C. and the still head showed 390° C. The distillate above 300° C. resembled the red oil of coal tar in appearance and odor but contained paraffin wax. The residue from this distillation formed, on cooling, a brittle coal-like substance melting above 200° C. It may be of interest to mention that the behavior of this oil above 250° C. is similar to that of the oils boiling in the same temperature range obtained in the hydrogenation of Alberta coals.

Summary

Considering the results of this series of experiments as a whole, it is probable that 75% of Alberta bitumen may be converted easily to gasoline and oil.

Of the remainder, 10% appears as gaseous hydrocarbons and the other 15% of asphaltic material is very resistant to both cracking and hydrogenation. Experiment No. 1-3 shows that a proper catalyst offers hope in reducing this material. Another and promising possibility is afforded by the anomalous result recorded in Experiment No. 3-2. The pitch residue had been reduced in this instance to 10% of the original bitumen by hydrogenation at 450° C. of an oil containing considerable non-asphaltic material. The significance of this result will be determined by further work on residues of various initial boiling points and by experiments in an apparatus that will allow of continuous removal of the gasoline fraction as formed.

The hydrogen absorption in the last three experiments when considered with the hydrogen absorption in the primary experiments, shows a total absorption by bitumen of 3% or more. Part of this appeared in the gaseous hydrocarbons but nevertheless this figure shows definitely that the theoretical capacity of the bitumen is not very much greater than its practical capacity for hydrogen.

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REVIEWS AND NOTES

Some New Physico-chemical Apparatus

I. A "Volumestat"

A simple apparatus for automatically maintaining a constant volume and registering its pressure is shown connected, for simplicity of description, with a constant volume gas thermometer (Fig. I). It has proved to be a very convenient addition to such thermometers as well as being entirely satisfactory in connection with the measurement of the velocity of gas reactions at constant volume—the purpose for which it was designed. Other applications of this apparatus will be indicated and discussed in a later paper.

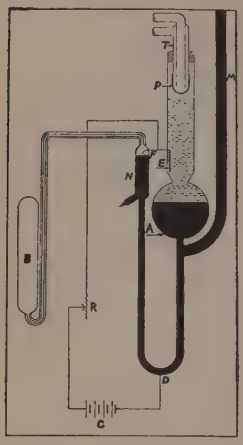

FIG. 1. *Gas thermometer and "volumestat"*

In Fig. 1 the gas thermometer bulb B is shown connected as usual to a manometer M and a mercury reservoir A. Instead, however, of balancing pressure changes in B by raising or lowering A, this is done by having the pressure above the mercury in A automatically adjusted so that the volume of the gas in B is kept constant and its pressure is registered on the manometer M. Increase of pressure in A is brought about by the electrolytic production of hydrogen and oxygen while decrease of pressure is accomplished by the recombination of these gases at the surface of a platinum catalyst.

The mechanism of this pressure adjustment is as follows: when increase of pressure in B forces the mercury away from the platinum point F the circuit $CRFD$ is broken and a potential sufficient to electrolyze the dilute H_2SO_4 above the mercury in A is established between the platinum anode E and the surface of the mercury in A. The hydrogen and oxygen thus produced force the mercury up in M and N until contact with F is again made and the evolution of gas ceases. The current in the circuit $CREAD$ is adjusted at the beginning of the experiment by means of the rheostat R so that the rate of production of hydrogen and oxygen is about twice that of their recombination on the platinum catalyst P. This is easily accomplished by setting R so that when the temperature of B is constant the times of "make" and "break" at F are approximately equal. This time can be made of the order of one or two seconds for apparatus or electrodes of any dimensions by adjusting the area and temperature of the platinum catalyst, the voltage of the battery C, or the strength of the H_2SO_4 in A. The times of "make" and "break" can be estimated by putting an ammeter in the circuit or simply by noting the change of shape of the mercury meniscus in A. When a current of suitable strength has been established the movement of the mercury meniscus at F is too small to be detected—an important circumstance in connection with the sensitivity of the thermometer.

When the times of "make" and "break" at *F* have been roughly equalized for any pressure in *B*, fluctuations in this pressure are taken care of as follows: for increase of pressure (rise of temperature) the ratio of the times of "make" and "break" at *F* becomes less than one, *i.e.*, hydrogen and oxygen are produced at a greater rate than they combine; for decrease of pressure (fall of temperature) the ratio becomes greater than one, *i.e.*, hydrogen and oxygen combine at a greater rate than they are produced. That the speeds of these reactions are more than sufficient to keep up with ordinary pressure or temperature changes will be shown in a later paragraph.

The platinum catalyst is prepared as follows: a paint of platinic chloride in oil of rosemary and oil of lavender is made up as described by Taylor (1). The end of the glass tube *T* is dipped into this paint and heated slowly in a Bunsen flame until a conducting film or mirror of platinum is obtained covering an area of the tube equal to that of the catalyst desired. This area may vary within wide limits without appreciably affecting the operation of the apparatus. More than one coat of paint may be necessary in order to produce a continuous film. This film is then made the cathode in a solution of platinic chloride and platinized as in the preparation of electrodes for conductivity measurements. The black uniform deposit of platinum thus obtained has been found to be a sufficiently active catalyst even at 0° C. It is deposited on the tube *T* so that its temperature and hence activity may be regulated by passing water at any desired temperature through the tube.

In earlier forms of the apparatus attempts were made to recombine the gases by means of a heated platinum wire or by a non-cooled surface of platinum black or platinized asbestos. The first scheme was abandoned on account of the frequency with which explosions occurred even in the presence of a large excess of nitrogen as diluent. The second was also unsatisfactory on account of the large variation of catalytic activity with temperature—the rate of combination increasing rapidly as the catalyst became warmed by the reaction. The method described above of keeping the catalyst at a definite temperature completely eliminates these difficulties and makes possible an exact control of the rate of recombination. In practice it has been found that a fairly large catalyst surface kept at the temperature of tap water is much more convenient than a small surface kept at a higher temperature. Any variation of catalytic activity due to the condensation of freshly formed water on the platinum surface has never been observed to interfere with the accuracy of the volume control.

A test of the apparatus may be quoted as an example of its operating efficiency. The temperature of the thermometer bulb, which was immersed in a 3-litre beaker of water stirred by a current of air, was raised from 15 to 100° C. in about 15 min. without any appreciable change in the "make/break" ratio. That is, the ammeter in the circuit continued to oscillate regularly at about one-second intervals between 0.4 amperes (circuit *CRFD*) and 0.2 amperes (circuit *CREAD*). Thus a large reserve of flexibility, so to speak, still remained. At no time could any movement of the meniscus at *F* be detected, so small was the volume change needed to make and break the small, low tension (*C* was

10 volts) current, nor was there any irregularity in the movement of the mercury in the manometer. The above was also true when the bulb was cooled in an even shorter time from 100 to 20° C.

About 5% sulphuric acid has usually been employed in this apparatus although its strength may obviously vary within wide limits. The same is true of the power input, which, however, must be roughly dependent on the activity of the catalyst and the rate at which the apparatus is to be operated. Because of oxidation the mercury must be made the cathode in the electrolysis although low voltage A.C. has been satisfactorily used. No instance of catalyst poisoning has so far been observed nor has any explosion occurred with a water cooled catalyst working up to pressures as high as three atmospheres.

The author is indebted to Prof. C. B. Nickerson for helpful criticism and for making photographs of the diagrams.

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II. A Combined Gas Heater and Thermoregulator

A simple combined heater and regulator of Pyrex glass which makes it possible to use gas for internal heating of a large glass thermostat is shown diagrammatically in Fig. 2. The mercury in the regulator bulb *R* opens and closes the main gas inlet *A* to the burner *B*. A small hole *E* in the side of the tube *A* serves as a by-pass to supply just enough gas to keep *B* always lighted. Air for the flame at *B* is supplied through *D*. If the laboratory is not supplied with compressed air a tight fitting glass tube may be slipped into or over the chimney *C* and attached to a water pump the speed of which is regulated so that the flame at *B* is colorless. The flame is started by shutting off the air supply and lighting the gas at the top of *C*. The air is then slowly turned on and, if the size of the jet at *B* makes it necessary, the gas is turned down. The blue cone in the flame at the chimney top increases until it finally strikes back with a loud whistling report and burns quietly at *B*. It is easy with a little practice in regulating the air and gas to keep the flame from being extinguished by the force of the striking down explosion. When *B* has been lighted the air-gas ratio must be adjusted until the yellow in the flame just disappears. Otherwise the inside of the chimney will become coated with soot and the apparatus will give off the disagreeable odor of a struck down Bunsen flame. When the desired temperature is reached and the regulator begins to operate, further adjustment of air and gas may be necessary to eliminate the odor of partial combustion.

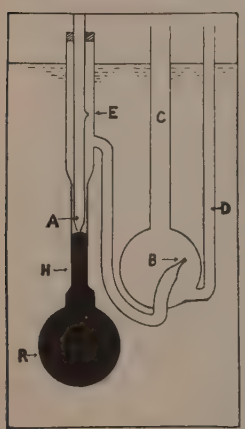

FIG. 2. *Heater-regulator*

The apparatus is entirely satisfactory for temperatures above 35 or 40° C. Below this temperature the water from the flame tends to condense in the

chimney and run back into the bulb *B* where it will eventually extinguish the flame. This may be avoided by running a capillary glass tube down the chimney to the bottom of *B* and attaching it to a water pump. Any water that collects is thus continually removed.

The range of the apparatus is readily changed by slipping the tube *A* up or down through its stopper or by changing the amount of mercury in *R*. *E* must obviously be made near the bottom of *A* if the temperature of the apparatus is to be changed over a wide range without extinguishing the flame to add or remove mercury. *E* is easily made and its size adjusted by drawing out a fine capillary from the side of *A* cutting it off close to the main tube and partially closing it in a small flame.

The sensitivity of the apparatus is obviously dependent on the volume of *R* and the diameter of the mercury column opening and closing *A*. One instrument during a trial experiment held the temperature of a 3-litre battery jar of water stirred by a current of air at 61.80° C. ($\pm 0.05°$) for 12 hr. without any readjusting. In this apparatus, which was not designed to be particularly sensitive, the volume of *R* is about 150 cc. (Pyrex Erlenmeyer flask) and the diameter of *H* about 1 cm.

If it is desired to utilize the heat of the flame more completely the chimney *C* may be bent in the form of a coil or zigzag. Non inflammable liquids with a high coefficient of expansion may be used together with mercury in the regulator by extending the tube *H* to dip into mercury at the bottom of *R*.

An obvious advantage of this internal over external gas heating is its freedom from the disturbing influence of air currents.

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Interim Report on Bacillus Calmette-Guérin

Introduction

Early in 1925 the National Research Council appointed an Associate Committee on Tuberculosis to draw up a comprehensive program of tuberculosis research. This led to the extension of several researches already under way and to the undertaking of research on several additional problems in human and animal tuberculosis. In this work the Council gratefully acknowledges the financial assistance of the Sun Life Assurance Company of Canada and the co-operation in research of the Alberta and Dominion Departments of Agriculture, Fort Qu'Appelle and Queen Alexandra Sanatoria, and the universities of Alberta, McGill, Montreal, Queen's and Toronto.

As a part of this investigation the committee has for over five years carried on researches on "B.C.G.", a bacillus developed for use as a vaccine against tuberculosis by Calmette and Guérin of the Pasteur Institute, Paris. At a meeting of the committee held in Ottawa, April 17-18, 1931, reports were presented covering the work to date on B.C.G., and an outline was drawn up

of supplementary researches recommended. At this meeting the committee unanimously authorized the publication of the following report, which may be taken as embodying the committee's tentative conclusions.

The National Research Council has had the privilege of publishing in the Canadian Journal of Research several papers descriptive of work done in this co-operative investigation. (Rankin, 1: 48-85; Mitchell and Duthie, 2: 406-408; Reed and Rice, 4: 389-398.) Others are to be published in the near future.

Bacillus Calmette-Guérin

1. B.C.G. represents a strain of bovine tubercle bacillus of reduced virulence and pathogenicity.

2. B.C.G. has acquired relatively fixed characters as to its virulence when maintained upon a specific medium (bile potato medium).

3. This relative avirulence may be maintained when B.C.G. is grown upon Sauton's medium or glycerinated potato; but as a precautionary measure, it may be returned to the bile potato medium at repeated intervals,—these intervals being at present unknown.

4. Under artificial conditions the virulence of B.C.G. may be enhanced by various cultural means, quite apart from the question of possible contamination of cultures.

5. When cultivated under the conditions of paragraph 3, B.C.G. is by many investigators regarded as innocuous to experimental animals on first passage, but others claim that occasionally it may become pathogenic.

6. When cultivated under the conditions of paragraph 4, B.C.G. may exhibit both virulence and pathogenicity.

Immunity

1. It is evident that much work remains to be done before the problem of vaccinal immunity is solved.

2. The use of B.C.G. as a vaccine, particularly when applied parenterally, confers a degree of resistance. This is determined by the absence of lesions or by the reduced extent and rate of development of the tuberculous process arising from natural or experimental infection.

3. The evidence available indicates that the degree of resistance diminishes from year to year.

4. The period of maximum resistance following vaccination, the rate of decrease of resistance and the results of revaccination have not been determined.

5. It is recognized that there is a possibility of a carrier state appearing in vaccinated animals.

Proposals for Future Work

1. The determination of a standard medium or media containing the elements which maintain a constant avirulence for the production of a stable vaccine.

2. A study of all the factors which enhance the virulence of the attenuated strain.

3. A study of the factors which, when utilizing stabilized vaccines, may effect the alteration of the virulence and pathogenicity of the organism in experimental animals.

4. A study of the factors governing variation of the organism in relation to possible enhancement of virulence in the animal (apart from highly virulent strains).

5. A study of other attenuated strains and cultures for the production of living vaccines.

6. A comparative study of the resistance induced by living and dead vaccines.

7. The determination of the duration of the increased resistance after vaccination.

8. That further investigations be instituted into the carrier question.

H. M. TORY
President, National Research Council of Canada.

MAY 11, 1931.

Note on Plant Breeding Abstracts

The Imperial Bureau of Plant Genetics has begun to issue a publication entitled "Plant Breeding Abstracts" in which all the more important current publications dealing with plant breeding and the genetics of crop plants are listed. The references are classified according to subject and each reference is followed by an abstract indicating the subject matter of the paper and the results obtained. The papers are divided into two halves, those published in the British Empire and those published in foreign countries. Papers written in foreign languages are usually abstracted somewhat more fully than papers in English.

"Plant Breeding Abstracts" is issued quarterly and Vol. I. No. 3. which was published on April 1, 1931 contains 197 references covering 52 pages.

The annual subscription for the publication is at present 5/- post free, single copies being obtainable at the price of 1/6. Subscriptions should be sent to the Deputy Director, Imperial Bureau of Plant Genetics, School of Agriculture, Cambridge, England.

P. S. HUDSON
Deputy Director.

APRIL 30, 1931.